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Syntheses of Nitrogen-containing Heterocyclic Compounds. XXVIII.[1] The Reissert Reaction of 4,6-Phenanthroline

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Reissert compounds (II to XI) were obtained by the application of potassium cyanide and acyl chloride to 4,6-phenanthroline (I) in dichloromethane and water. Reaction of I with silver cyanide and benzoyl chloride afforded the Reissert compounds (XI to XIII), and XIII had an amino group. Reaction of XI with methanol or ethanol gave the Reissert compound XII or XIV. Reaction of XV, XVI, and XVII with potassium cyanide and benzoyl chloride gave compounds (XVIII to XXII).

This Reissert reaction was examined by Hückel's approximation and its results on Reissert compounds obtained agreed approximately with experimental results.

Keywords——4,6-phenanthroline; benzo[*f*][1,7]naphthyridine; 1,9-diazaphenanthrene; Reissert reaction; Hückel's molecular orbital; Henze's reissert reaction

As a part of studies on nitrogen-containing heterocyclic compounds and following the chemical reaction of 4,6-phenanthroline (I) reported earlier,[3] we have further examined the Reissert reaction of I and its N-oxides[3] and the regio-selectivity in this Reissert reaction[4-6] was examined by Hückel's molecular orbital (HMO) method.

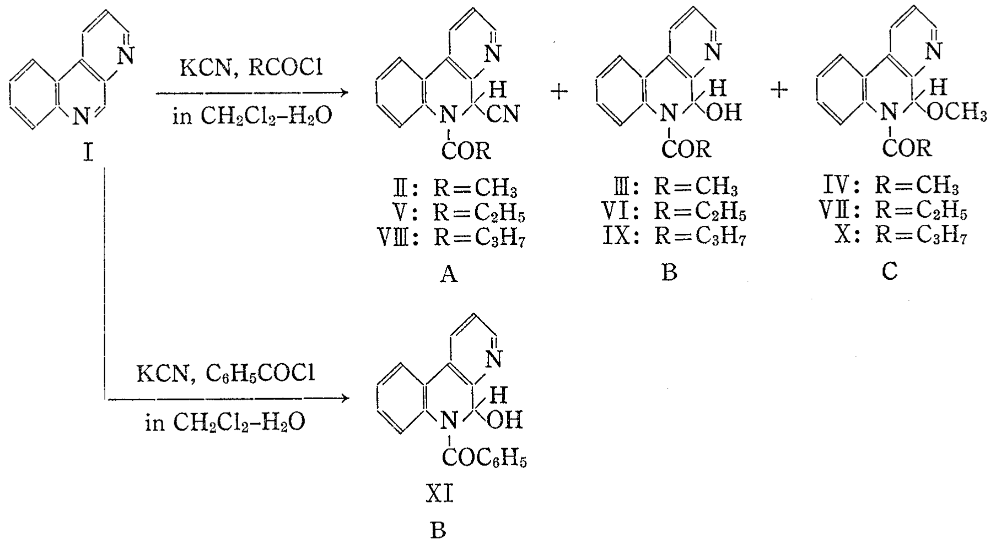

Chart 1

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[1] Part XXVII: Y. Hamada, M. Sugiura, *Yakugaku Zasshi*, **98**, 1 (1978).

[2] Location: *a*) *Yagoto-Urayama, Tenpaku-ku, Nagoya, 468, Japan*; *b*) *31 Ooka 2-chome, Minami-ku, Yokohama, 233, Japan.*

[3] Y. Hamada and I. Takeuchi, *Chem. Pharm. Bull.* (Tokyo), **24**, 2769 (1976).

[4] F.D. Popp, "Adv. Heterocycl. Chem.," Vol. 9, ed. by A.R. Katritzky and A.J. Boulton, Academic Press, New York, 1968, pp. 1—25.

[5] Y. Hamada, I. Takeuchi, and H. Matsuoka, *Chem. Pharm. Bull.* (Tokyo), **18**, 1026 (1970).

[6] I. Takeuchi and Y. Hamada, *Chem. Pharm. Bull.* (Tokyo), **24**, 1813 (1976).

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We reported previously5) that the reaction of 1,6-naphthyridine with potassium cyanide and acid chloride (RCOCl; R$=$CH$_3$, C$_2$H$_5$, C$_3$H$_7$) in dichloromethane-water system resulted in the reaction with the nitrogen in 5-position and gave a Reissert compound with cyano group in 6-position, whereas reaction with benzoyl chloride gave a Reissert compound with cyano and hydroxyl groups, while the same reaction with 1,7-naphthyridine6) resulted in reaction with the nitrogen in 7-position to form the Reissert compound with a cyano group in 8-position. Therefore, in order to see the effect of R group in RCOCl, reaction of I with potassium cyanide and RCOCl (R$=$CH$_3$, C$_2$H$_5$, C$_3$H$_7$, and C$_6$H$_5$) in dichloromethane-water system was carried out, and Reissert compounds (II to XI), illustrated in Chart 1, were obtained. These compounds can be divided into three types of A (II, V, VIII), B (III, VI, IX, XI), and C (IV, VII, X). Among the A-type compounds, structure of VIII was determined as 6-butyryl-5,6-dihydro-4,6-phenanthroline-5-carbonitrile from its elemental analytical values ($C_{17}H_{15}N_3O$), mass spectrum (MS) *m/e* 277 (M$^+$), 207 (M$^+$—HCOC$_3$H$_7$), and infrared (IR) spectral data $\nu_{\max}^{\text{KBr}}$ 1670 cm^{-1} (N–C=O), and from its nuclear magnetic resonance (NMR) spectral data listed in Table I.

TABLE I. NMR Spectral Data of Reissert Compound

compd. No.	Chemical shift (δ)								Coupling constants (Hz)		
	1H	2H	3H	5H	OH	OCH$_3$	–OCH$_2$	–CH$_3$	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
II a)	8.12	7.44	8.52	7.06					8.0	1.5	4.0
III b)	8.42	7.52	8.54	6.70	6.70				8.0	2.0	4.0
IV a)	8.12	7.36	8.52	6.60		3.44			8.0	2.0	4.0
V a)	8.10	7.40	8.50	7.04					8.0	2.0	5.0
VI b)	8.42	7.40	8.52	6.68	6.68				8.0	2.0	4.0
VII a)	8.16	7.36	8.56	6.64		3.44			8.0	2.0	5.0
VIII b)	8.42	7.40	8.52	6.68	6.68				8.0	2.0	4.0
IX a)	8.16	7.34	8.54	6.02		3.48			8.0	2.0	4.0
XI a)	8.48	7.54	8.52	6.46	6.68				8.0	2.0	4.0
XII b)	8.16	7.54	8.54	6.70			3.88	1.06	8.0	2.0	5.0
XIII a)	8.0	7.28	8.54	7.0			2.76(NH$_2$)		8.0	2.0	4.0
XIV a)	8.20	7.36	8.56	6.56				3.52	8.0	2.0	5.0
XVIII a)	9.08	8.00	7.24						8.0	2.0	4.0
XX a)	8.96	8.00		9.46					8.0	2.0	
XXII a)	9.20	8.40							8.0	2.0	
XXI a)	8.96	8.00		9.46					8.0	2.0	

a) In CDCl$_3$.
b) In DMSO-d_6.

In B-type compounds, IX was determined as 6-butyryl-5,6-dihydro-4,6-phenanthroline-5-ol, from its elemental analytical values ($C_{16}H_{16}N_2O_2$), MS *m/e* 268 (M$^+$), IR $\nu_{\max}^{\text{KBr}}$ 1665 cm^{-1} (N–C=O), and NMR [in (CD$_3$)$_2$SO] of double doublets at δ 8.25 for the proton at 3- and at δ 8.24 for that at 1-position, and a singlet at δ 6.60 for the overlapped proton at 5- and the hydroxyl, whose peak decreased on deuterization, as shown in Fig. 1.

In the C-type compounds, X was determined as 6-butyryl-5,6-dihydro-5-methoxy-4,6-phenanthroline from its elemental analytical values ($C_{17}H_{18}N_2O_2$), MS *m/e* 282 (M$^+$), 251 (M$^+$—OCH$_3$), 180 (251 — C$_3$H$_7$CO), IR $\nu_{\max}^{\text{KBr}}$ 1670 cm^{-1} (N–C=O), and from its NMR signals (in CDCl$_3$) showing double doublets at δ 8.54 for proton at 3- and δ 8.16 for that at 5-position, and as singlet at δ 3.44 for OCH$_3$ group.

The structure of other compounds (II to VII) were all determined from elemental analytical values and from mass, IR, and NMR spectral data. Presence of a hydroxyl group in

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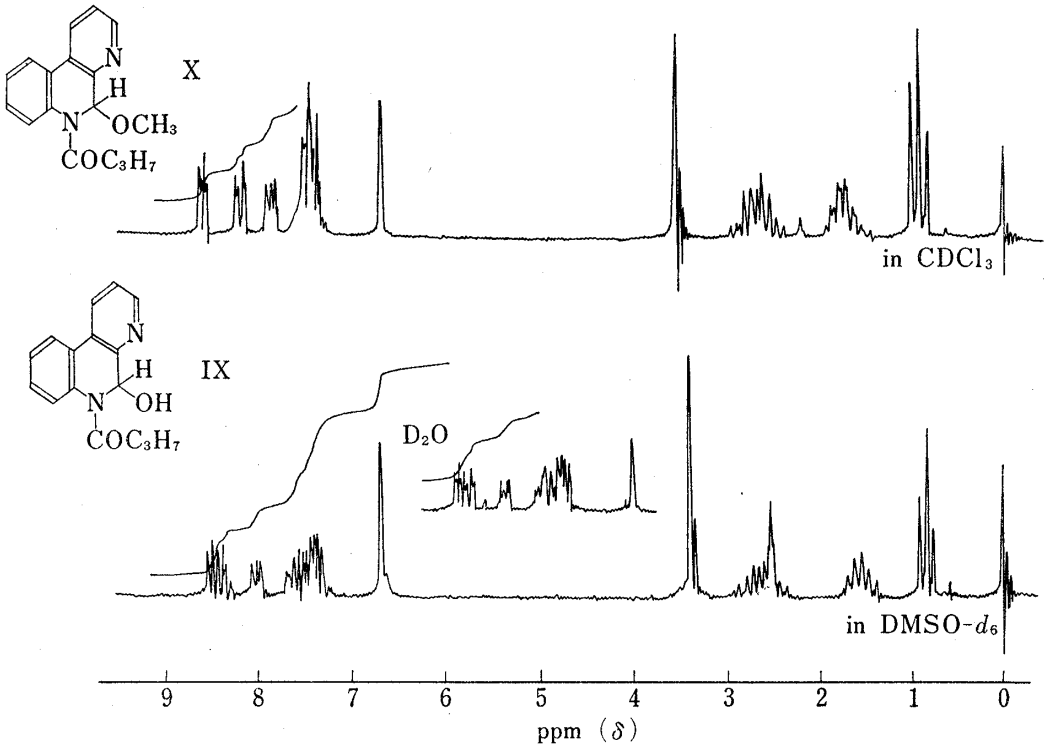

Fig. 1. NMR Spectra of IX and X

NMR spectra were taken with a JEOL-PS-100 (100 MHz) high resolution spectrometer.

5-position of B-type compounds was considered to be due to the introduction of hydroxyl before that of cyano, or replacement of cyano with hydroxyl, as reported by Off and others.[7]

Relationship between the relative yield of these A-, B-, and C-type compounds and the kind of solvent used was examined in detail. As shown in Table II, the yield of C-type methoxy compounds increased by the use of method (a), *i.e.*, with a small amount of water, while the yield of A- and B-type compounds increased when the amount of water was larger, *i.e.*, method (b). Reason for the formation of C-type compounds is still obscure and examination is now being made.

B-type compounds were obtained by the reaction of 1,6-naphthyridine[5] with potassium cyanide and benzoyl chloride. Kobayashi and Kumadaki[8] obtained the A-type cyano compound by using silver cyanide instead of potassium cyanide. Therefore, I was allowed to react with silver cyanide and benzoyl chloride in dichloromethane and, as shown in Chart 2, a C-type compound (XII) was obtained. The structure of XII was determined as 6-benzoyl-5-ethoxy-5,6-dihydro-4,6-phenanthroline from its elemental analysis ($C_{21}H_{18}N_2O_2$) MS *m/e* 330 (M^+), IR ν_{max}^{KBr} 1665 cm^{-1} (N–C=O), and NMR data shown in Table I.

The same reaction of I with silver cyanide and benzoyl chloride was then carried out in anhydrous chloroform and a different compound (XIII) was obtained in 3% yield. The structure of XIII was determined as 5-amino-6-benzoyl-5,6-dihydro-4,6-phenanthroline, similarly from its elemental analysis ($C_{19}H_{15}N_3O$) MS *m/e* 301 (M^+), and IR ν_{max}^{KBr} 3320 and 3322 cm^{-1} (NH_2). Formation route of this compound was assumed to be as shown in Cahrt 2.

Refluxing of XI with methanol or ethanol gave the methoxy (XIV) or ethoxy (XII′) compound in around 87% yield. The structure of XIV was determined as 6-benzoyl-5-meth-

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[7] *a*) B.C. Off, T.R. Kershaw, and S.R. Chabra, *Tetrahedron Lett.*, **1969**, 1687; *b*) F.D. Popp, personal communication.

[8] Y. Kobayashi and I. Kumadaki, *Chem. Pharm. Bull.* (Tokyo), **17**, 2144 (1969).

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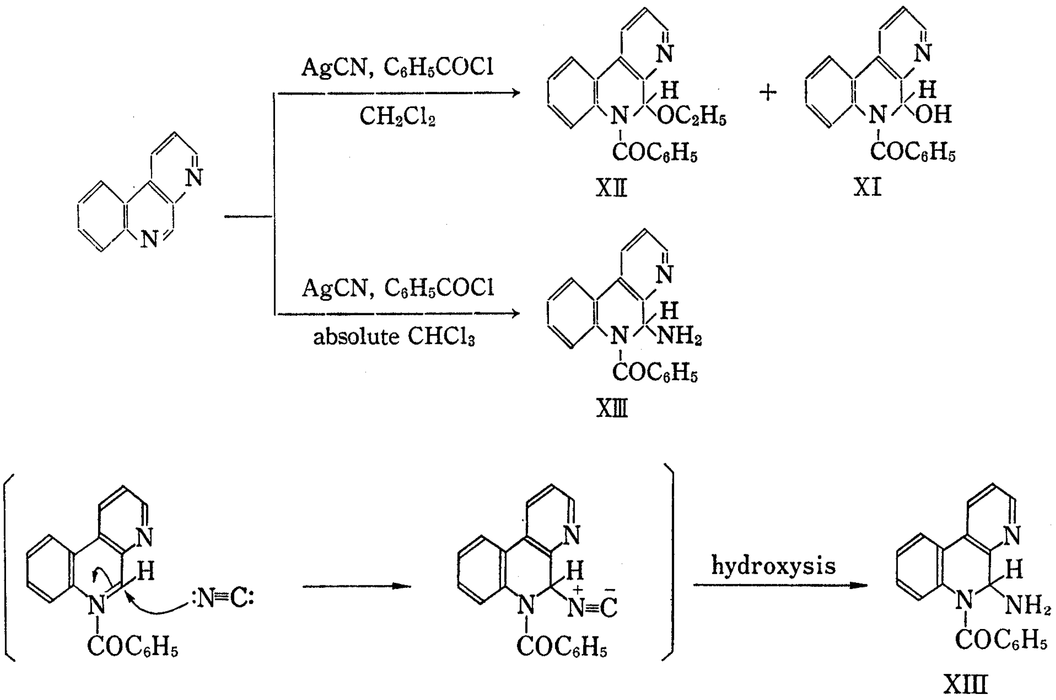

Chart 2

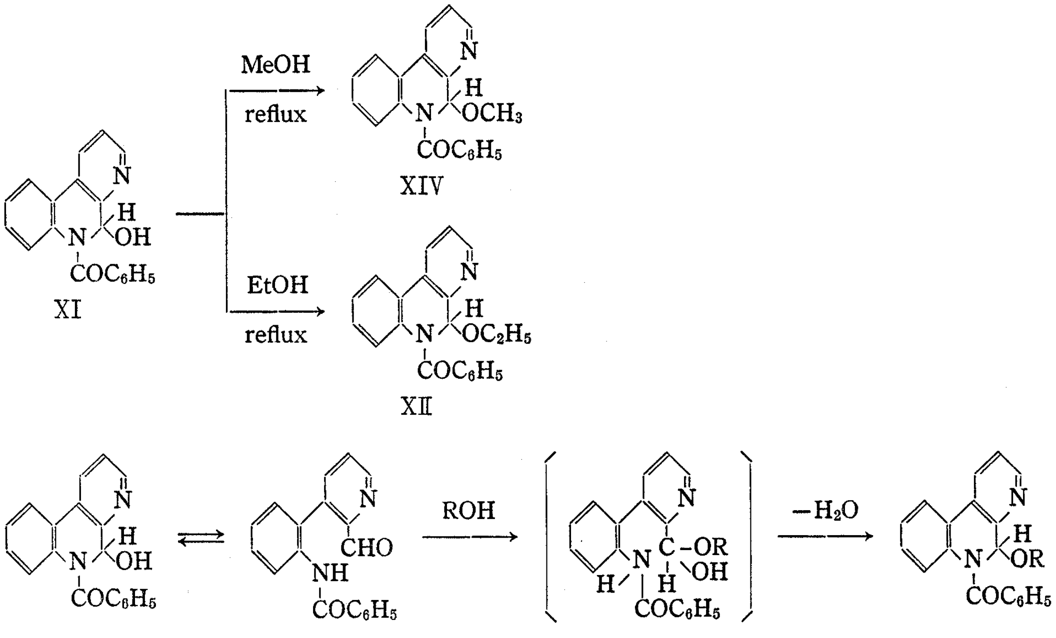

Chart 3

oxy-5,6-dihydro-4,6-phenanthroline from its elemental analysis ($C_{20}H_{16}N_2O_2$), MS m/e 316 (M^+), and IR ν_{max}^{KBr} 1650 cm^{-1} (N–C=O). The compound (XII′) was found to be identical with XII obtained as above, by mixed fusion test and comparison of their IR spectra.

Considering the report of Elliott[9] that application of benzoyl chloride and 10% sodium hydroxide to quinoline resulted in the isolation of an aldehyde compound formed by its ring fission, formation of XII and XIV probably passed through an intermediate formation of a hemiacetal by ring fission followed by recyclization with dehydration.

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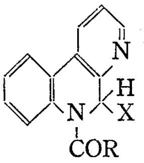
[9] I.E. Elliott, *J. Org. Chem.*, **34**, 305 (1969).

TABLE II

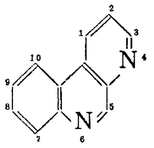
RCOCl	Reaction method	Yields (%) of three types of products		
		A	B	C
CH_3	a	Trace	16.2	20.0
	b	2.9	37.5	2.4
C_2H_5	a	Trace	5.9	26.9
	b	1.8	35.5	4.7
C_3H_7	a	Trace	22.4	22.4
	b	3.3	3.37	11.2

a = CH_2Cl_2 : H_2O (5:1).
b = CH_2Cl_2 : H_2O (2:1).

TABLE III.



and

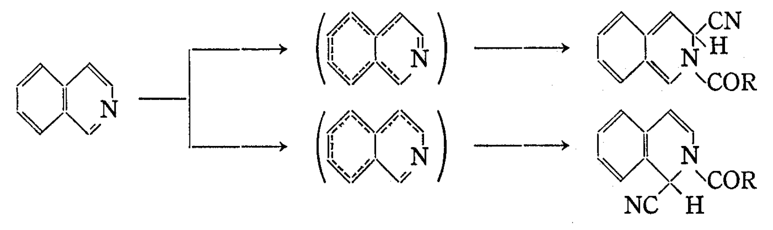


Compound No.	R	X	C_3	C_5	mp (°C)	Appearance	Formula	Analysis (%) Calcd. (Found)			Mass Spectrum m/e (M+)
								C	H	N	
II	CH_3	CN			196—198	White prisms	$C_{15}H_{11}N_3O$	72.27 (72.52)	4.45 (4.64)	16.86 (16.91)	249 (M^+) 210 180
III	CH_3	OH			178—179	White prisms	$C_{14}H_{12}N_2O_2$	69.99 (69.81)	5.03 (5.29)	11.66 (11.81)	238 (M^+) 199 180
IV	CH_3	OCH_3			138—140	Colorless needles	$C_{15}H_{14}N_2O_2$	70.85 (70.91)	5.55 (5.74)	11.02 (11.31)	254 (M^+) 223
V	C_2H_5	CN			176—178	White needles	$C_{16}H_{13}N_3O$	72.98 (72.84)	4.98 (5.11)	15.96 (15.81)	263 (M^+) 207 180
VI	C_2H_5	OH			190—191	White prisms	$C_{15}H_{14}N_2O_2$	70.85 (70.90)	5.55 (5.70)	11.02 (11.80)	254 (M^+)
VII	C_2H_5	OCH_3			101—103	White prisms	$C_{16}H_{16}N_2O_2$	72.62 (71.85)	6.01 (6.28)	10.44 (10.65)	268 (M^+) 238 180
VIII	C_3H_7	CN			151—152	White needles	$C_{17}H_{15}N_3O$	73.63 (73.68)	5.54 (5.70)	15.15 (15.43)	277 (M^+) 207 180
IX	C_3H_7	OH			181—183	Colorless needles	$C_{16}H_{16}N_2O_2$	71.62 (71.80)	6.01 (6.28)	10.44 (10.64)	268 (M^+)
X	C_3H_7	OCH_3			133—134	Colorless needles	$C_{17}H_{18}N_2O_2$	72.32 (72.46)	6.43 (6.65)	9.92 (9.81)	282 (M^+) 251 180
XI	C_6H_5	OH			220—222	White prisms	$C_{19}H_{14}N_2O_2$	75.48 (75.73)	4.67 (4.84)	9.27 (9.41)	302 (M^+) 197 180
XIV	C_6H_5	OCH_3			185—187	White prisms	$C_{20}H_{16}N_2O_2$	75.93 (75.85)	5.10 (4.86)	8.86 (8.71)	316 (M^+) 285
XVIII				CN	160—162	White needles	$C_{13}H_7N_3$	76.08 (76.25)	3.44 (3.62)	20.28 (20.11)	
XX			CN		192—193	White needles	$C_{13}H_7N_3$	76.08 (76.30)	3.44 (3.50)	20.28 (20.51)	
XXII			CN	CN	213—214	Yellow needles	$C_{14}H_6N_4$	73.03 (73.26)	3.63 (3.81)	24.34 (24.52)	

Finally, Henze's report[10] that the Reissert reaction of quinoline 1-oxide gave quinaldonitrile in a good yield was examined with phenanthrolines, as shown in Chart 4. The reaction of 4,6-phenanthroline 4-oxide[3] (XV) with potassium cyanide and benzoyl chloride in dichloromethane-water system afforded compounds XVIII and XIX in a respective yield of 47.9% and 33.3%. The structure of XVIII was determined as 5-cyano-4,6-phenanthroline from its analytical values ($C_{13}H_7N_3$), MS *m/e* 205 (M^+), and IR $\nu_{\max}^{\text{KBr}}$ 2210 cm^{-1} (C≡N). The reaction of XV with benzoyl chloride in dichloromethane gave XIX′ in 65% yield. Compound (XIX′) was found to be identical with 4,6-phenanthrolin-5(6*H*)-one (XIX), obtained earlier,[11] by mixed fusion test and identity of IR spectra. The same reaction of 4,6-phenanthroline 4-oxide (XVI) afforded XX and XXI in 38 and 25% yield, respectively. The structure of XX was determined as 3-cyano-4,6-phenanthroline from its molecular formula ($C_{13}H_7N_3$), MS *m/e* 205 (M^+), and IR $\nu_{\max}^{\text{KBr}}$ 2210 cm^{-1} (C≡N), as well as from NMR data given in Table I, and that of XXI as 4,6-phenanthrolin-3(4*H*)-one, similarly from analytical and spectral data ($C_{12}H_8N_2O$; *m/e* 196 (M^+), IR $\nu_{\max}^{\text{KBr}}$ 1663 cm^{-1} (N–C=O)). Finally, 4,6-phenanthroline 4,6-dioxide[3] (XVII), was allowed to react with potassium cyanide and benzoyl chloride in dichloromethane and 5.3% of XXII was obtained with 50% recovery of XVII. The structure of XXII was

TABLE IV

Starting material Localized model of double bond Expected product



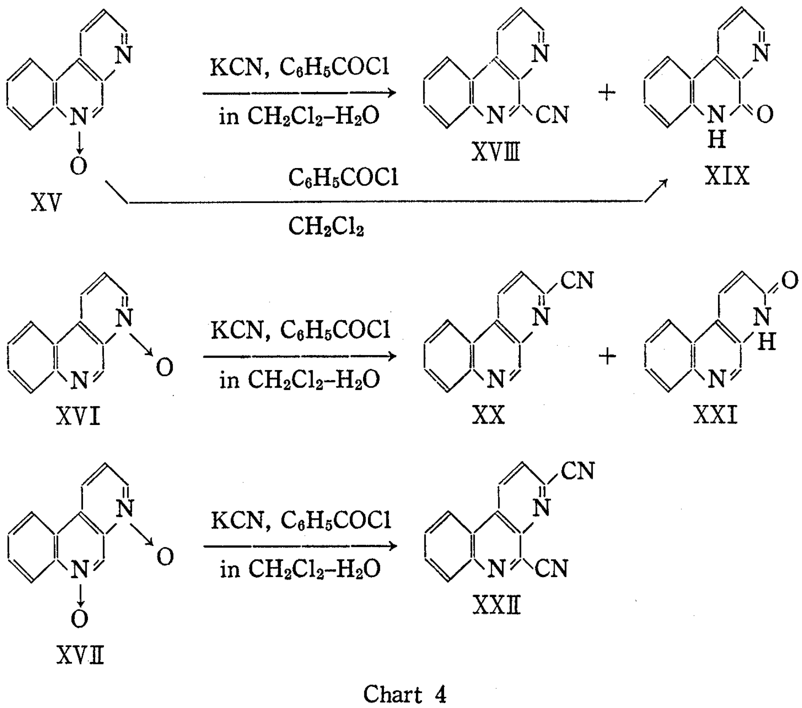


Chart 4

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[10] A. Henze, *Ber.*, **69**, 1566 (1936).

[11] Y. Hamada, I. Takeuchi, and M. Hirota, *Chem. Pharm. Bull.* (Tokyo), **22**, 486 (1974).

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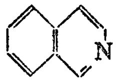
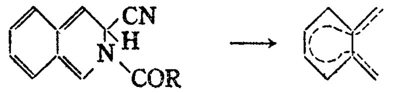
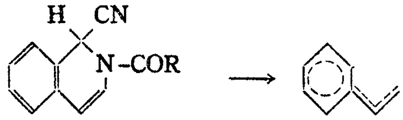
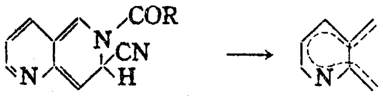
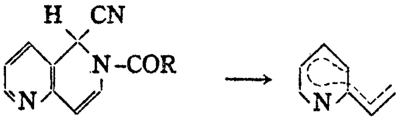
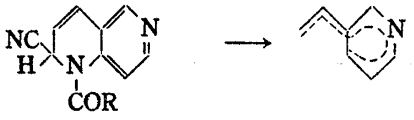
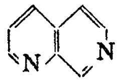
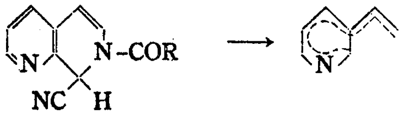
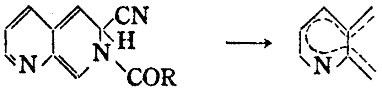
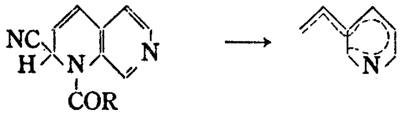
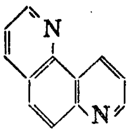
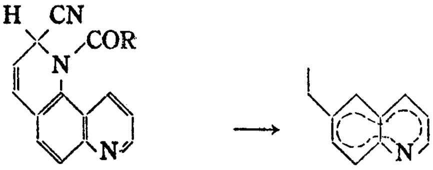
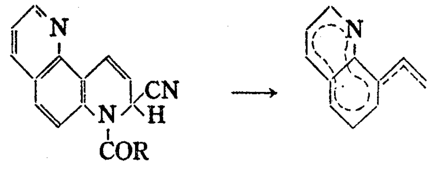
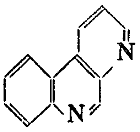
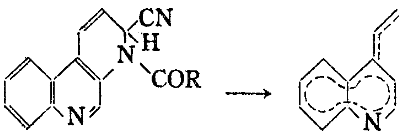
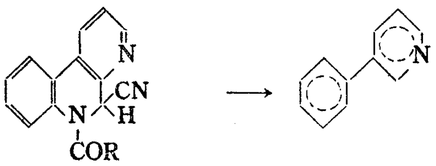
TABLE V

Starting material	Possible localized models	π-Electron energy (β-unit)	Order of expected product	Experimental product
	① 	10.05828	②>①	②
	② 	10.52692		
	③ 	10.92344	④>⑤>③	④
	④ 	11.38548		
	⑤ 	11.37670		
	⑥ 	11.3820	⑧≧⑥>⑦	⑥
	⑦ 	10.93184		
	⑧ 	11.384		
	⑨ 	17.077	⑩>⑨	⑩
	⑩ 	17.093		
	⑪ 	17.10	⑫>⑪	⑫
	⑫ 	17.341		

Parameters $\alpha_N = \alpha_0 + 0.6\beta$.
The carbon atom adjacent to the nitrogen atom.
$\alpha_{C'} = \alpha_0 + 0.1\beta_0$
$\beta_{CC} = \beta_{CN} = \beta$

determined as 3,5-dicyano-4,6-phenanthroline, similarly from elemental and spectral analyses ($C_{14}H_6N_4$, *m/e* 230 (M^+), IR ν_{max}^{KBr} 2211 cm^{-1} (C≡N)). Formation of carbostyril compounds, like XIX, from these N-oxides is considered to be the same as the process for formation of carbostyril from quinoline 1-oxides.[12]

Estimation of the Site of Reaction and Orientation by HMO Method

The question of the orientation of compounds; *e. g.*, direction of the Reissert reaction of heterocycles having at most one nitrogen atom in a ring, such as in isoquinoline, 1,6- and 1,7-naphthyridines, 4,6-phenanthroline, and 1,7-phenanthroline, and the question of the position of the Reissert reaction when there are two nitrogen atoms in one ring were examined by HMO method. Since the Reissert reaction may be considered as an addition reaction to the double bond in one species of C=N, activation energy ($\Delta E\pi$) was calculated by assuming a transition state, in which the double bond at the addition site is no longer conjugated to the rest of the π-system. This calculation would, at the same time, compare the stability of the π-system in the addition products formed.

As shown in Table IV, up to four localized models are possible when there are two nitrogen atoms in a ring but, among them, the π-electron energy was calculated for other localized models and, assuming that those with a large stabilization energy would be like to be practical, reaction site and orientation were estimated. For this calculation, the following parameters were used: $\alpha_N=\alpha_0+0.6\beta$, where, $\alpha_C,=\alpha_0+0.1\beta_0$ and $\beta_{CC}=\beta_{CN}=\beta$ for the carbon atom adjacent to the nitrogen atom. This result is shown in Table IV, in which the π-electron energy ($E\pi-n\alpha_0$) is expressed in β_0 unit, and the site with the largest value of this unit is assumed hence, it reflects the $E\pi$ of the corresponding transition state. As shown in Table V, a good agreement was found between the obtained HMO energies and the experimental results.

As shown above, the use of benzoyl chloride as RCOCl in the Reissert reaction of 4,6-phenanthroline was found to give a result different from those of 1,6- and 1,7-naphthyridines.

Experimental[13]

6-Acyl-5,6-dihydro-4,6-phenanthrolines (II to X)——A solution of 0.0051 mol of KCN dissolved in 1 ml of H_2O was added to a solution of 0.0017 mol of 4,6-phenanthroline (I) dissolved in 5 ml of CH_2Cl_2, the mixture was stirred, and 0.0034 mol of acid chloride was added during 30 min. The mixture was further stirred for 4—6 hr and CH_2Cl_2 layer was separated. The aqueous layer was washed with two 10 ml portion of CH_2Cl_2 and the combined organic layer was washed consecutively with two 5 ml portions of H_2O, 5% HCl, H_2O, 5% NaOH, and finally with H_2O, dried over $MgSO_4$, and filtered. The solvent was evaporated, the residue dissolved in benzene was chromatographed over silica gel, and the column was eluted with $CHCl_3$.

The first effluent fraction, recrystallized from benzene–cyclohexane (1:1), gave A-type compounds, II, V, and VIII.

The second fraction, recrystallized from $CHCl_3$: $(CH_3)_2CO$ (1: 1), gave the B-type compounds, III, and IX.

The third fraction, recrystallized from EtOH, gave the C-type compounds, IV, VII, and X. Details of these products are given in Table I and III.

6-Benzoyl-5,6-dihydro-4,6-phenanthrolin-5-ol (XI)——To a mixture of 0.3 g of I, 15 ml of CH_2Cl_2, 0.3 g of KCN, and 1 ml of H_2O, 0.47 g of BzCl was added during 2 hr. The reaction mixture was treated by the same method as in the case of II to X. The residue was recrystallized from $CHCl_3$ to give 0.27 g (54%) of XI. Details of XI are given in Tables I and III.

The Reissert Reaction of I——a) To a mixture of 0.3 g of I, 0.476 g of BzCl, and 20 ml of CH_2Cl_2, 0.49 g of AgCN was added and the mixture was stirred for 2 hr at 15°. The solid substance formed was filtered off, the filtrate was washed with 1 N NaOH solution, and CH_2Cl_2 layer was dried over K_2CO_3. After CH_2Cl_2 was evaporated, the residue was dissolved in benzene and purified through a column of silica gel (20 g). The first effluent fraction was recrystallized from benzene to 250 mg (50%) of 6-benzoyl-5-ethoxy-5,6-dihydro-4,6-phenanthroline (XII) as white needles, mp 168—170°. MS *m/e*: 930 (M^+). IR ν_{max}^{KBr} 1665 cm^{-1} (N–CO).

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12). E. Ochiai and C. Kaneko, *Chem. Pharm. Bull.* (Tokyo), 7, 191 (1959).

13) All melting points are not corrected.

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Anal. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.45. Found: C, 76.51; H, 5.30; N, 8.59. Its NMR spectrum (Table I).

The second effluent fraction was recrystallized from EtOH to 10 mg (20%) of XI as white prisms, mp 220—222°. Compound (XI) was identified with XI synthesized as above.

b) To a mixture of 0.3 g (0.0017 mol) of I, 0.476 g (0.0034 mol) of BzCl, and 20 ml of absolute $CHCl_3$, 0.49 g of AgCN was added in N_2 stream, and the mixture was stirred for 12 hr at 15°. The reaction mixture was treated in the same way as in method (a) and the reeidue was recrystallized from benzene to give 15 mg (3%) of 5-amino-6-benzoyl-5,6-dihydro-4,6-phenanthroline (XIII) as white needles, mp 192—193°. IR ν_{max}^{KBr} 3320 and 3322 cm^{-1} (NH_2). MS *m/e*: 301 (M^+). *Anal.* Calcd. for $C_{19}H_{15}N_3O$: C, 75.73; H, 5.02; N, 13.95. Found: C, 75.91; H, 5.40; N, 13.81. Its NMR spectrum (Table I).

Reaction of XI with Methanol or Ethanol——A solution of 100 mg (0.003 mol) of XI in 10 ml of MeOH or EtOH was refluxed for 1—4 hr and the solvent was evaporated. The residue was recrystallized from $(CH_3)_2CO$ or MeOH to give XIV (89 mg, 86%) or XII (95.1 mg, 87%) as white needles. Physical data of these compounds are given in Table I and III.

The Reissert Reaction of 4,6-Phenanthroline 6-Oxide (XV)——a) To a mixture of 300 mg (0.0015 mol) of XV, 5 ml of CH_2Cl_2, 1 g (0.045 mol) of KCN, and 1 ml of H_2O, 0.42 g (0.003 mol) of BzCl was added during 30 min. The mixture was further stirred for 6—8 hr and CH_2Cl_2 layer was separated. The aqueous layer was extracted with two 10 ml portion of CH_2Cl_2 and the combined organic layer was washed consecutively with two 5 ml portion of H_2O, 5% HCl, H_2O, 5% NaOH, and H_2O dried over $MgSO_4$, and filtered. The solvent was evaporated, and the residue was chromatographed over silica gel, and the column was eluted with $CHCl_3$. The first effluent fraction gave 100 mg (33.3%) of XIX as white needles, mp over 300° (EtOH). The second fraction gave 150 mg (47.9%) of XVIII as needles mp 160—162° (cyclohexane). Details of XVIII are given in Tables I and II. Compound (XIX) was identified with 4,6-phenanthrolin-5(6*H*)-one synthesized by another method,[3] by mixed mp and by comparison of their IR and NMR spectra.

b) To a mixture of 300 mg (0.0015 mol) of XV and 5 ml of CH_2Cl_2, 0.42 g (0.003 mol) of BzCl was added during 30 min and the mixture was treated as in method (a). Recrystallization of the residue from EtOH gave 200 mg (65%) of XIX′ which was identical with XIX obtained as above.

The Reissert Reaction of 4,6-Phenanthroline 4-Oxide (XVI)——To a mixture of 300 mg (0.0015 mol) of XVI, 5 ml of CH_2Cl_2, 1 g (0.0045 mol) of KCN, and 1 ml of H_2O, 0.42 g (0.003 mol) of BzCl was added during 2 hr. This reaction mixture was treated as in the case of XV. Recrystallization of the residue from EtOH first gave 4,6-phenanthrolin-3(4*H*)-one (XXI) as white needles, mp over 300°, Yield, 85 mg (25%). *Anal.* Calcd. for $C_{12}H_8N_2O$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.52; H, 3.95; N, 14.44. IR ν_{max}^{KBr} 1720 cm^{-1} (N–C=O). MS *m/e*: 196 (M^+). Its NMR spectrum (Table I).

The residue obtained after evaporation of the recrystallization solvent was dissolved in benzene and the solution was passed through a column of Al_2O_3. The effluent residue was recrystallized from EtOH to give 120 mg (38%) of XX as white needles, mp 192—193°. Details of XX are given in Table I and III.

The Reissert Reaction of 4,6-Phenanthroline 4,6-Dioxide (XVII)——To a mixture of 200 mg (0.00094 mol) of XVII, 5 ml of CH_2Cl_2, 0.184 g (0.0028 mol) of KCN, and 1 ml of H_2O, 0.26 g (0.0018 mol) of BzCl was added during 2 hr and this reaction mixture was treated in the same way as in the case of XV. The residue was chromatographed over silica gel and the column was eluted with $CHCl_3$.

The first fraction gave 100 mg (50%) of XVII′ [EtOH–H_2O (1:1)], which was found to be the recovered XVII.

The second fraction gave 12 mg (5.3%) of XXII as yellow needles, mp 213—214° [benzene–cyclohexane (1:1)]. IR ν_{max}^{KBr} 2215 cm^{-1} (CN). MS *m/e*: 230 (M^+). Compound (XXII) was identified as 5,6-dicyano-4,6-phenanthroline from its NMR spectra. Details of XXII are shown in Tables I and II.I

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