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Studies on Tertiary Amine Oxides. LXIV.[1] Reaction of 4-Nitroquinoline 1-Oxide and Related Compounds with Potassium Cyanide

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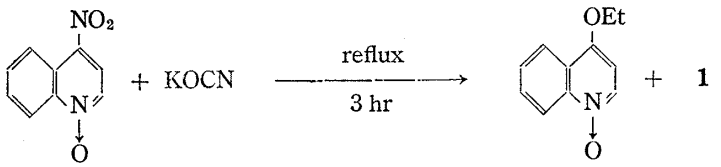
Treatment of 4-nitroquinoline 1-oxide (**1**) with potassium cyanate in hot ethanol afforded 4-ethoxyquinoline 1-oxide. On the other hand when potassium cyanide was applied instead of the cyanate, the reaction followed an alternate course giving 3-cyano-4-quinolinol (**3**). Compound **3** was produced also from reactions in 90% ethanol, DMF, DMSO and dioxane, the best yield being obtained from the reaction in DMF at 80—90°. It was further disclosed that besides **1**, 2-chloro- (**13**), 2-bromo-4-nitroquinoline 1-oxides (**14**), 4-nitroquinoline (**18**) and 2-bromo-4-nitroquinoline (**19**) underwent the same type of reaction.

Keywords——nucleophilic reaction; The von Richter reaction; 3-cyano-4-quinolinol; 3-cyano-1,4-dihydroquinoline; bis-(3-quinolylmethyl)amine; solvent effect

A previous paper has described that treatment of quinoline 1-oxides with potassium cyanate and tosyl chloride in ethanol produces ethyl N-(2-quinolyl)carbamates.[3] These results prompted us to attempt the reaction of 4-nitroquinoline 1-oxide with potassium cyanate using ethanol as solvent in the hope of introducing ethoxycarbonylamino group into the 4-position. The anticipated reaction did not occur; however a new type of reaction was encountered when potassium cyanide instead of the cyanate was applied to 4-nitroquinoline 1-oxide.

When an ethanol solution of 4-nitroquinoline 1-oxide (**1**) and potassium cyanate was refluxed for 3 hr, 4-ethoxyquinoline 1-oxide (**2**)[4] was isolated in 54.2% yield accompanied by 42.1% recovery of **1**. Since potassium cyanate is not sufficiently soluble in ethanol, the reaction using 80% ethanol as solvent was attempted under the similar conditions, but practically the same result was obtained, no expected 4-ethoxycarbonylamino derivative being detected.



1 **2**

in anhyd. EtOH	54.1%	42.1%
in 80% EtOH	53.3%	35.3%

The nucleophilic displacement of the 4-nitro group of **1** thus occurred, but the introduced group was ethoxy group and potassium cyanate apparently behaved as a base; such behavior of ethoxy group as a nucleophile in the presence of cyanate ion was previously observed in the reaction of quinaldine 1-oxide with potassium cyanate and tosyl chloride in ethanol.[3]

1) Part LXIII: H. Saito and M. Hamana, *Yakugaku Zasshi*, in press.
2) Location: *3-1-1, Maidashi, Higashi-ku, Fukuoka, 812, Japan.*
3) M. Hamana and S. Kumadaki, *Chem. Pharm. Bull.* (Tokyo), **23**, 2284 (1975).
4) E. Ochiai, M. Ishikawa, and Z. Sai, *Yakugaku Zasshi*, **63**, 280 (1943).

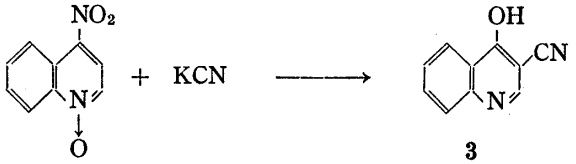
In order to avoid the participation of ethanol, a solution of **1** and potassium cyanate in dimethylformamide (DMF) was heated at 80—90° for 6 hr, but only **1** was recovered in 81.6% yield, no definite product being detected.

In connection with the above reaction, the reaction of **1** with potassium cyanide was examined. At first, anhydrous ethanol solution of **1** and the cyanide was refluxed for 5 hr and 3-cyano-4-quinolinol (**3**), colorless needles, mp 297—298°, was obtained in a low yield of 15.7% together with 31.6% recovery of **1**.

Although product **3** has a nitrile group (IR ν_{max}^{Nujol} cm^{-1}: 2250) and its empirical formula, $C_{10}H_6N_2O$, is the same with that of 4-cyanoquinoline 1-oxide (mp 189—190°)[5], **3** is obviously not identical with the latter compound. Its structure was unambiguously elucidated by the reaction sequence shown in Chart 1. Bredereck *et al.*[6] have described the synthesis of **3** by refluxing ethyl β-anilino-α-cyanoacrylate in biphenyl ether, but did not record its melting point.

Subsequently in exploring the features of the reaction, various conditions were examined and the results listed in Table I were obtained.

Table I. Reaction of 4-Nitroquinoline 1-Oxide (**1**) with Potassium Cyanide



1 **3**

Reaction conditions			Yield of **3** (%)	Recov. **1** (%)
Solvents	Temp.	Time (hr)		
Anhy. EtOH	Reflux	5	15.7	31.6
90% EtOH	Reflux	6	23.5	—
48% EtOH	Reflux	20	—	—
MeOH	Reflux	5	—	—
DMF	80—90°	5	81.4	—
DMF	R.T.[a]	5	49.0	—
DMSO	30—40°	5	39.2	—
DMSO	R.T.[a]	3	25.5	—
Dioxane	80—90°	5	2.0	—

a) Room temperature.

While the reaction occurred also in 90% ethanol giving **3** in somewhat better yield of 23.5%, ethanol is apparently not essential for the proceeding of the reaction, and the use of DMF and dimethylsulfoxide were more favorable for the formation of **3**, the reaction in DMF at 80—90° giving the best yield of 81.4%. Dioxane was less effective than ethanol as the reaction medium, and attempted reactions under the conditions of von Richter reaction[7] gave no definite product expect for the reaction in 90% ethanol.

Chart 1 formulated reactions carried out in connection with the structural elucidation of product **3**.

5) *a*) E. Ochiai and T. Naito, *Yakugaku Zasshi*, **65A** (5, 6), 3 (1945); *b*) H.U. Daeniker and J. Druey, *Helv. Chim. Acta*, **41**, 2148 (1958).
6) H. Bredereck, F. Effenberger, H. Botsch, and H. Rehn, *Chem. Ber.*, **98**, 1081 (1965).
7) *a*) V. von Richter, *Ber.*, **4**, 21, 459, 553 (1871); *b*) *Idem, ibid.*, **7**, 1145 (1874); *c*) *Idem, ibid.*, **8**, 1418 (1875); *d*) J.F. Bunnet, J.F. Cormack, and F.C. McKey, *J. Org. Chem.*, **15**, 481 (1950).

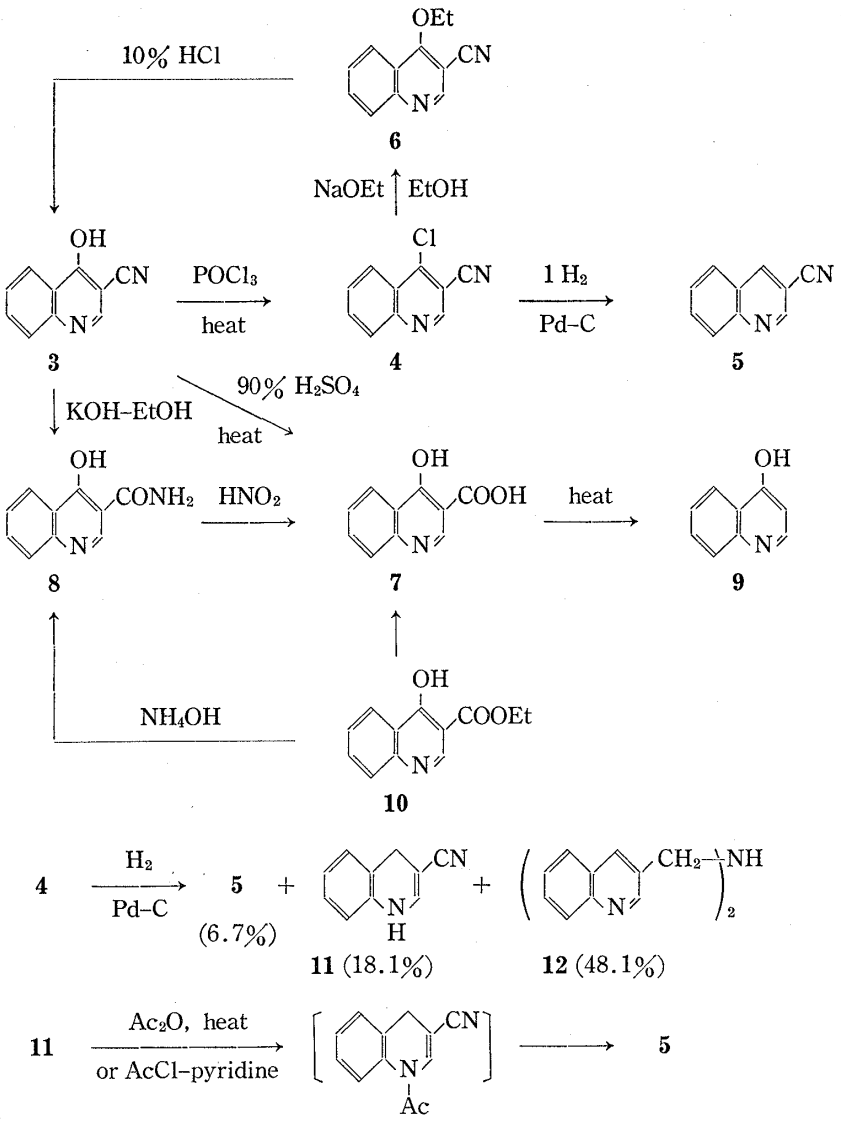


Chart 1

Heating **3** with phosphoryl chloride gave 4-chloro-3-cyanoquinoline (**4**), which was converted separately into the known 3-cyanoquinoline (**5**)[8] by hydrogenation with one molar equivalent of hydrogen over 10% palladium-charcoal and into the 4-ethoxy derivative (**6**) upon treatment with ethanolic sodium ethoxide; hydrolysis of **6** with 10% hydrochloric acid regenerated **3**. Hydrolysis of **3** with hot 90% sulfuric acid afforded 3-carboxy-4-quinolinol (**7**). This was proved identical with an authentic sample obtained by hydrolysis of 3-ethoxycarbonyl-4-quinolinol (**10**) prepared from aniline and diethyl ethoxymethylenemalonate,[9] and underwent decarboxylation upon heating at 270—280° (bath temp.) to 4-quinolinol (**9**). On the other hand, hydrolysis with ethanolic potassium hydroxide led to 3-carboxyamido-4-quinolinol (**8**), which was identical with the product prepared from **10** by heating with ammonia, and was transformed into compound **7** upon treatment with nitrous acid.

The above-mentioned hydrogenation of **4** to **5** was effected with one molar equivalent of hydrogen in the presence of the 10% amount of the catalyst. On the other hand, when the two- or three-fold amount of the catalyst was used and the reaction was continued untill

8) H. Gilman and S.M. Spatz, *J. Am. Chem. Soc.*, **63**, 1553 (1941).
9) G.F. Duffin and J.D. Kendal, *J. Chem. Soc.*, **1948**, 893.

the uptake of hydrogen markedly slowed down, 3-cyano-1,4-dihydroquinoline (**11**) and bis-(3-quinolylmethyl)amine (**12**) were formed in the respective yields of 18.1 and 48.7% besides **5** (6.7%). The similar reduction of **5** also produced **11** and **12**.

Product **11** forms colorless prisms of mp 130°, and its structure was confirmed by the elemental analysis, the infrared (IR) absorptions at 3260 and 2220 cm^{-1} indicative of a secondary amine and a nitrile group, respectively, a maximum in the ultraviolet spectrum at 328 nm, and by the direct comparison with an authentic sample prepared from **5** by sodium borohydride reduction according to the procedure reported by Yamada and his co-workers[10]. Heating **11** with acetic anhydride or treating with acetyl chloride in pyridine gave not N-acetate but instead 3-cyanoquinoline **5**, and an attempted Diels-Alder reaction with furane failed, **11** being recovered almost quantitatively. Although **12** was an oil and could not crystallize, its structure was well deduced from the IR absorption at 3320 cm^{-1} attributed to a secondary amine, its transformation to N-tosyl derivative, $C_{27}H_{23}N_2O_2S$, and the nuclear magnetic resonance (NMR) spectrum of the tosylate.

Further, 2-chloro-(**13**)[11] and 2-bromo-4-nitroquinoline 1-oxides (**14**)[11] were found to undergo the same type of reaction. Treatment of **13** with potassium cyanide at 30—40° in DMF for 5 hr led to the formation of 2-chloro-3-cyano-4-quinolinol (**15**) in 41.0% yield, no visible sign of the replacement of the active 2-chloro substituent with cyano group being noticed. From the reaction of **14**, the corresponding 2-bromo derivative (**16**) was similarly obtained in 40.0% yield. Both compounds, **15** and **16**, were transformed upon heating with phosphoryl chloride into the same 2,4-dichloro-3-cyanoquinoline (**17**) which was identified by the direct comparison with an authentic sample prepared by the Gabriel method[12]; apparently the concomitant replacement of the 2-bromo group occurred in the latter case.

In exploring the role of the N-oxide function in the above-mentioned reactions, 4-nitroquinoline (**18**) was treated with potassium cyanide in DMF at 60° for 5 hr and it was disclosed that the same type of reaction took place smoothly and product **3** was formed in 62.7% yield. Similarly 2-bromo-4-nitroquinoline (**19**) gave **16** in 53.5% yield. Accordingly, the presence of the N-oxide function is conceivably not essential for the initiation of the reaction, though the details of its deoxygenation are not yet clear.

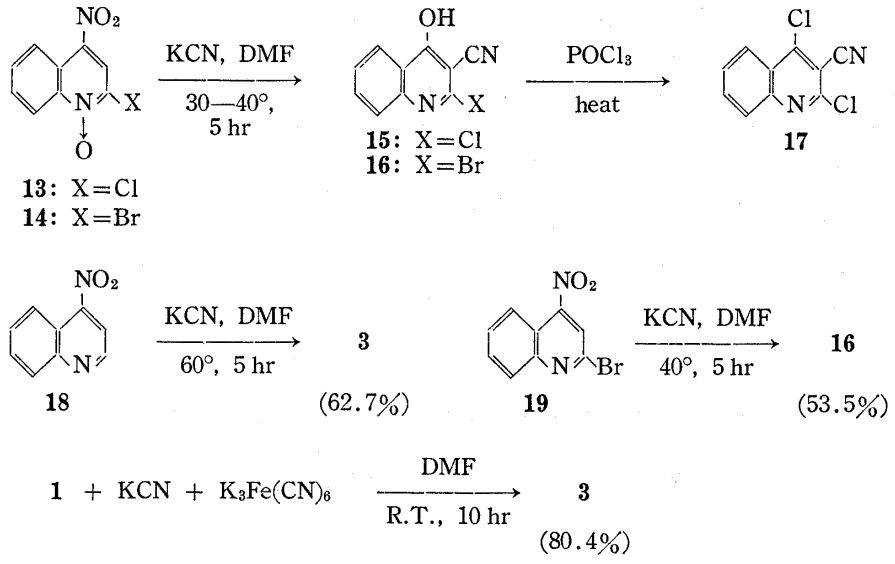


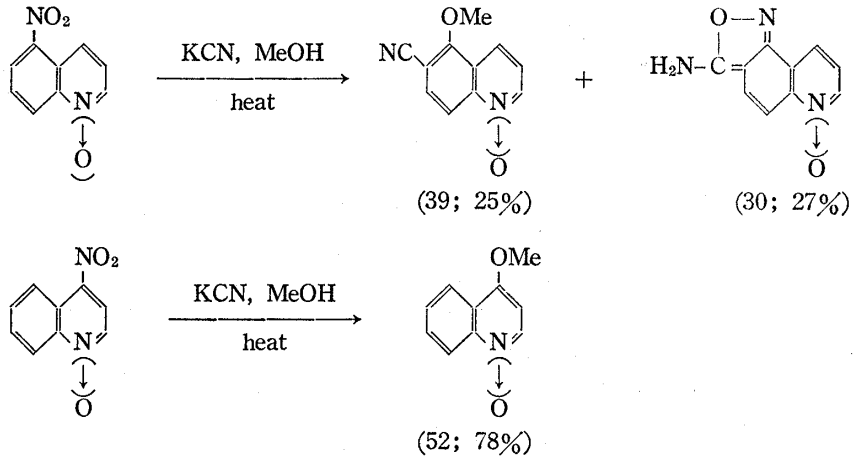
Chart 2

10) Y. Kikugawa, M. Kuramoto, I. Saito, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **21**, 1914 (1973).
11) M. Yamazaki, N. Honjo, K. Noda, and M. Hamana, *Yakugaku Zasshi*, **86**, 749 (1066).
12) S. Gabgriel, *Ber.*, **51**, 1500 (1918).

With an aim to gain a product having N-oxide group, the reaction of **1** in the presence of potassium ferricyanide as an oxidizing agent was tried, but resulted in the formation of **3** as the sole product in the same way as that without an oxidizing agent.

These results are shown in Chart 2.

Okamoto and *et al.*[13,14] have described that treatment of nitroquinoline derivatives with potassium cyanide in hot methanol generally leads to methoxycyano- and aminoisoxazoloquinolines as exemplified below, but reactions of 4-nitroquinoline (**18**) and its N-oxide (**1**) follow an alternate course and resulted in only nucleophilic replacement of 4-nitro group with methoxy group.



As mentioned above, while the reaction of **1** with potassium cyanate in ethanol produced 4-ethoxyquinoline 1-oxide **2** in the same manner as that with potassium cyanide in methanol, the reaction with potassium cyanate in ethanol gave not 4-ethoxy compound **2** but 3-cyano-4-quinolinol **3**. The reason is not clear at all why such a striking difference is observed between the reaction of **1** with potassium cyanide in methanol and that in ethanol.

The formation of 3-cyano-4-quinolinols from 4-nitroquinolines is distinctly different from the von Richter reaction[7] and the reaction reported by Okamoto *et al.*[13,14] Although the reaction should be considered to be initiated by nucleophilic attack of cyanide anion at the 3-position of 4-nitroquinolines, the details of the mechanism have not been established, particularly with respect to the origin of the hydroxy group introduced into the 4-position. It seems quite unlikely that the hydroxy substituent is derived from the oxygen atom of solvent used or from water present in the reaction media; especially when anhydrous solvents were used, the participation of water is apparently unreasonable. There may be conceivable an attractive path which involves the participation of an oxygen atom of the nitro group such as for instance the intermediacy of oxazirane. In any event, further studies are needed to elucidate the essential features and the mechanism of the reaction.

Experimentals[15]

Reaction of 4-Nitroquinoline 1-Oxide (1) with KOCN——1) A mixture of **1** (1.90 g), KOCN (1.62 g) and EtOH (30 ml) was refluxed for 3 hr. EtOH was evaporated and H_2O was added to the residue, which was extracted with $CHCl_3$. The extract was passed through an alumina column to give successively 0.80 g (42.1%) of **1** and 1.23 g (54.2%) of 4-ethoxyquinoline 1-oxide (**2**) dihydrate, colorless needles, mp40—41° (aq. ether).

13) *a*) T. Okamoto and H. Takahashi, *Chem. Pharm. Bull.* (Tokyo), **16**, 1700 (1968); *b*) T. Okamoto, H. Takahashi, H. Takayama, T. Kitagawa, and M. Ikeda, *Chem. Pharm. Bull.* (Tokyo), **17**, 140 (1969).
14) T. Okamoto and H. Takahashi, *Chem. Pharm. Bull.* (Tokyo), **19**, 1809 (1971).
15) All melting and boiling points are uncorrected. NMR spectra were measured with JNM-3H-60 spectrometers at 60 MHz using trimethylsilane (TMS) as internal reference.

2) To 80% EtOH (25 ml) was added 1 (1.90 g) and KOCN (1.62 g), and the whole was refluxed 2 hr. Similar work up gave 1.20 g (53.3%) of 2 dihydrate and 0.67 g (35.3%) of 1.

3) To DMF (20 ml) was added 1 (1.90 g) and KOCN (1.62 g), and the whole was heated on a water-bath for 6 hr. DMF was evaporated, H_2O was added to the residue, which was extracted with $CHCl_3$ to give 1.55 g (81.6%) of 1.

Reaction of 1 with KCN——1) A mixture of 1 (0.57 g), KCN (0.585 g) and anhyd. EtOH (30 ml) was refluxed for 5 hr. The reaction mixture was evaporated, and H_2O was added to the residue, which was extracted with $CHCl_3$ to give 0.18 g (31.6%) of 1. The mother liquor from $CHCl_3$ extraction was treated with active charcoal and weakly acidified with 10% HCl to give precipitates. Recrystallization from MeOH gave 0.08 g (15.7%) of 3-cyano-4-quinolinol (3), colorless needles, mp 297—298°. *Anal.* Calcd. for $C_{10}H_6N_2O$: C, 70.58; H, 3.55; N, 16.48. Found: C, 70.58; H, 3.50; N, 16.59. IR ν_{max}^{Nujol} cm^{-1}: 2250 (C≡N).

2) To a solution of 1 (0.57 g) in DMF (10 ml) was added with stirring KCN (0.39 g) and the reactants were heated at 80—90° with agitating for 5 hr. The reaction mixture was concentrated under reduced pressure, and H_2O was added to the residue, which was extracted with $CHCl_3$. No product was obtained from the extract. The mother liquor from $CHCl_3$ extraction was weakly acidified with 10% HCl to deposit crystalls, which were filtered and recrystallized from MeOH to give 0.415 g (81.4%) of 3.

Reaction of 3 with $POCl_3$——A mixture of 3 (0.10 g) and $POCl_3$ (3 ml) was refluxed for 3 hr, concentrated under reduced pressure and ice-water was added to the residue. Deposited crystals were filtered and washed successively with 10% Na_2CO_3 and H_2O. Recrystallization from *n*-hexane or acetone gave 0.10 g (90.1%) of 3-cyano-4-chloroquinoline (4), colorless needles, mp 129—130°. *Anal.* Calcd. for $C_{10}H_5ClN_2$: C, 63.66; H, 2.65; N, 14.85. Found: C, 63.26; H, 2.75; N, 14.82. IR ν_{max}^{Nujol} cm^{-1}: 2220 (C≡N).

Reduction of 4——1) A solution of 4 (0.50 g) and AcONa (0.22 g) in EtOH (20 ml) was hydrogenated at ordinary temperature and pressure over 10% Pd-C (0.05 g). After uptake of 1 equivalent amount of hydrogen the filtrate from the catalyst was concentrated under reduced pressure and H_2O was added to the residue, which was made alkaline with $NaHCO_3$ and extracted with $CHCl_3$. The extracted fraction was chromatographed on alumina with ether to give 0.23 g (56.4%) of 3-cyanoquinoline (5),[8] colorless needles, mp 106—108° (ether).

2) A solution of 4 (0.60 g) in EtOH (20 ml) was hydrogenated at ordinary temperature and pressure over 10% Pd-C (0.20 g). After uptake of 230 ml of hydrogen, the filtrate from the catalyst was concentrated under reduced pressure and H_2O was added to the residue, which was made alkaline with $NaHCO_3$ and extracted with $CHCl_3$. The extracted products were chromatographed on alumina. The first fraction eluted with ether gave 0.04 g (6.7%) of 5. The $CHCl_3$ effluent was recrystallized from acetone to afford 0.90 g (18.1%) of 3-cyano-1,4-dihydroquinoline (11),[10] colorless prisms, mp 130°. *Anal.* Calcd. for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.95; H, 5.28; N, 17.88. IR ν_{max}^{Nujol} cm^{-1}: 3260 (N–H), 2220 (C≡N), 1640 (C=C). UV λ_{max}^{EtOH} nm: 233.2, 328. From the last fraction eluted with MeOH, 0.23 g (48.7%) of bis-(3-quinolylmethyl)amine (12) was obtained as a viscous oil. IR ν_{max}^{Neat} cm^{-1}: 3320 (N–H). Treatment of 12 with TsCl in pyridine afforded 0.32 g of N-tosyl derivative, colorless pillars, mp 152° (acetone). *Anal.* Calcd. for $C_{27}H_{23}N_3O_2S$: C, 71.52; H, 5.08; N, 9.27. Found: C, 72.01; H, 5.25; N, 9.54. NMR (CF_3COOH solution) δ: 2.54 (3H, s, CH_3), 5.20 (4H, s, $2CH_2$), 7.64 (2H, d, J=8.1 Hz, 2 protons of phenyl ring), 8.06 (2H, d, J=8.1 Hz, 2 protons of phenyl ring), 8.20—9.60 (12H, m, aromatic protons of quinoline ring).

Reduction of 5——A solution of 5 (1.0 g) in MeOH (50 ml) was hydrogenated over Pd-C (0.30 g) as in the foregoing experiment to give 0.10 g (9.9%) of 11 and 0.48 g (49.5%) of 12 besides recovery of 5 (0.12 g, 12.0%).

Reactions of 11——1) A mixture of 11 (0.18 g) and Ac_2O (2 ml) was heated on a water-bath for 2 hr. The reactants were concentrated under reduced pressure and H_2O was added to the residue, which was made alkaline with K_2CO_3 and extracted with $CHCl_3$ to give 0.17 g (96.0%) of 5.

2) A solution of 11 (0.20 g) and AcCl (0.15 g) in pyridine (4 ml) was kept at room temperature overnight. The reactants were concentrated under reduced pressure and H_2O was added to the residue to deposit 0.15 g (76.1%) of 5.

Reaction of 4 with NaOEt——To NaOEt–EtOH (prepared from 0.10 g of Na and 15 ml of EtOH) was added 4 (0.80 g), and the whole was refluxed for 5 hr. The reaction mixture was evaporated *in vacuo* and H_2O was added to the residue, which was extracted with $CHCl_3$. The deposits insoluble in both H_2O and $CHCl_3$ were filtered and recrystallized from MeOH to give 0.035 g (4.8%) of 3. The $CHCl_3$ extract was evaporated and the residue was chromatographed on alumina with ether to afford 0.78 g (92.9%) of 3-cyano-4-ethoxyquinoline (6), colorless needles, mp 100—101°. *Anal.* Calcd. for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.09; N, 14.13. Found: C, 72.98; H, 5.20; N, 14.13. IR ν_{max}^{Nujol} cm^{-1}: 2240 (C≡N).

Hydrolysis of 4——A mixture of 4 (0.70 g) and 10% HCl (10 ml) was warmed at 50—60° for 5 min and cooled. The deposited crystals were recrystallized from MeOH to give 0.58 g (96.5%) of 3.

Hydrolysis of 3 with 90% H_2SO_4——A solution of 3 (0.29 g) in H_2SO_4 (2.9 ml) was heated on an oil-bath maintained at 140—160° for 3 hr. The cooled solution was poured on ice-water, and the deposited crystals were filtered and recrystallized from MeOH to afford 0.10 g (31.0%) of 3-carboxy-4-quinolinol (7).[9] *Anal.* Calcd. for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.41. Found: C, 63.10; H, 3.71; N, 7.50. The identity of 7 was established by comparison with an authentic sample prepared by hydrolysis of 3-ethoxycarbonyl-4-quinolinol (10).[9]

Decarboxylation of 7——Heating **7** (0.07 g) on an oil-bath maintained at 270—280° was continued until the evolution of CO_2 had ceased. The residue was recrystallized from MeOH to give 0.05 g (92.6%) of 4-quinolinol (**9**), colorless pillars, mp 202—203°.

Hydrolysis of 3 with KOH–EtOH——To a 10% KOH–EtOH (10 ml) was added **3** (0.37 g), and the whole was refluxed for 50 hr. The reaction mixture was concentrated under reduced pressure and H_2O was added to the residue, which was adjusted to pH 7.0 with 10% HCl. The deposited crystals were filtered and recrystallized from MeOH to give 0.20 g (48.9%) of 3-carboxyamido-4-quinolinol (**8**), colorless needles, mp 290°. *Anal.* Calcd. for $C_{10}H_8N_2O_2$: C, 63.82; H, 4.29; N, 14.89. Found: C, 63.64; H, 4.32; N, 14.73.

Preparation of 8 from 10——A mixture of **10** (0.33 g) and conc. NH_4OH (3 ml) was heated at 110—120° in a sealed tube for 5 hr. The reaction mixture was concentrated under reduced pressure and the residue was recrystallized from MeOH to give 0.26 g (89.6%) of **8**.

Reaction of 8 with HNO_2——A cooled solution of **8** (0.10 g) in conc. H_2SO_4 (1 ml) was treated with $NaNO_2$ (0.05 g), and then heated on a water-bath for 2 hr. The cooled solution was neutralized with Na_2CO_3 to deposit crystals. Recrystallization from MeOH afforded 0.05 g (50.0%) of **7**.

Reaction of 2-Chloro-4-nitroquinoline 1-Oxide (13) with KCN——A mixture of **13** (0.67 g), KCN (0.39 g) and DMF (10 ml) was stirred at 40° for 5 hr. The reaction mixture was evaporated under reduced pressure and H_2O was added to the residue, which was extracted with $CHCl_3$. The extract gave no product. The mother liquor from $CHCl_3$ extraction was neutralized with 10% HCl to deposit crystals. Recrystallization from MeOH gave 0.25 g (41.0%) of 2-chloro-3-cyano-4-quinolinol (**15**), colorless needles, mp 305° (decomp.). *Anal.* Calcd. for $C_{10}H_5ClN_2O$: C, 58.68; H, 2.44; N, 13.69. Found: C, 58.91, H, 2.33; N, 13.87. IR ν_{max}^{Nujol} cm^{-1}: 2250 (C≡N).

Reaction of 2-Bromo-4-nitroquinoline 1-Oxide (14) with KCN——A mixture of **14** (0.58 g), KCN (0.26 g) and DMF (10 ml) was stirred at 40° for 5 hr as in the foregoing experiment to give 0.22 g (40.0%) of 2-bromo-3-cyano-4-quinolinol (**16**), pale yellow needles, mp 298°. *Anal.* Calcd. for $C_{10}H_5BrN_2O$: C, 48.19; H, 2.01; N, 11.25. Found: C, 48.65; H, 2.11; N, 10.95. IR ν_{max}^{Nujol} cm^{-1}: 2246 (C≡N).

2,4-Dichloro-3-cyanoquinoline (17)——1) A mixture of **15** (0.10 g) and $POCl_3$ (1 ml) was refluxed for 5 hr. The reaction mixture was concentrated under reduced pressure and H_2O was added to the residue, which was made alkaline with Na_2CO_3 and extracted with $CHCl_3$ to give 0.11 g (100%) of **17**,[12] colorless needles, mp 164—165°. *Anal.* Calcd. for $C_{10}H_4Cl_2N_2$: C, 53.81; H, 1.79; N, 12.51. Found: C, 53.91; H, 1.85; N, 12.11.

2) The reaction of **16** with $POCl_3$ under the same conditions also gave **17** in quantitatively yield.

Reaction of 1 with KCN in the Presence of $K_3Fe(CN)_6$——To a solution of **1** (0.57 g) in DMF (15 ml) was added $K_3Fe(CN)_6$ (1.18 g) and KCN (0.80 g), and the reactants were stirred at room temperatures for 10 hr. Insoluble substances were filtered, and the filtrate was concentrated under reduced pressure and H_2O was added to the residue, which was extracted with $CHCl_3$ to furnished no definite product. The mother liquor from $CHCl_3$ extraction was neutralized with 10% HCl and the deposited crystals were recrystallized from MeOH to give 0.41 g (80.4%) of **1**.

Reaction of 4-Nitroquinoline (18) with KCN——A mixture of **18** (0.52 g), KCN (0.39 g) and DMF (10 ml) was stirred at 60° for 5 hr, and processed as described in the reaction of **1** to give 0.32 g (62.7%) of **3**.

Reaction of 2-Bromo-4-nitroquinoline (19) with KCN——A mixture of **19** (0.76 g), KCN (0.39 g) and DMF (15 ml) was stirred at 40° for 5 hr to afford 0.40 g (53.5%) of **16**.