  Bull. Chem. Soc. Jpn., 55, 2445—2449 (1982)

The Transition Metal-catalyzed *N*-Heterocyclization. A Reductive Transformation of Aminonitroarenes and Dinitroarenes into Phenanthroline Derivatives Using Aliphatic Aldehydes under Carbon Monoxide Pressure

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(Received December 21, 1981)

The Catalytic *N*-heterocyclization of aminoarenes and dinitroarenes using aliphatic n-C_3—C_5 aldehydes was carried out at 180 °C under the pressure of carbon monoxide (70 atm at room temperature) in the presence of $RhCl(PPh_3)_3$ and $PdCl_2$ as a binary catalyst system. The reaction of *p*-nitroaniline with propanal, butanal, and pentanal gave 3,8-diethyl-2,9-dimethyl-4,7-phenanthroline, 2,9-diethyl-3,8-dipropyl-4,7-phenanthroline, and 3,8-dibutyl-2,9-dipropyl-4,7-phenantroline in 43, 57, and 54% yields respectively. On the other hand, *m*-nitroaniline and *o*-nitroaniline gave 1,7-phenanthroline and imidazole derivatives in rather low yields (21 and 24%) under the reaction conditions employed.

Recently, novel methods have been developed for building up a quinoline nucleus using transition-metal complexes as catalysts under nonacidic conditions.[1,2] In previous papers, we have demonstrated that rhodium, ruthenium, and palladium complexes are effective catalysts for the *N*-heterocyclization of aminoarenes and nitroarenes.[3-6] μ,μ'-Dichlorobis(norbornadiene)dirhodium(I)($[RhCl(NBD)]_2$) was active for the *N*-heterocyclization of aminoarenes using aliphatic aldehydes.[3] Nitroarenes were reductively converted into quinolines and (dialkylamino)arenes using an aldehyde in the presence of a binary catalyst system, $RhCl(PPh_3)_3$–$PdCl_2$, under the pressure of carbon monoxide.[4] $RuCl_2(PPh_3)_3$ is also active for the *N*-heterocyclization of aminoarenes using $\Delta^{2,3}$-unsaturated alcohols[5] and for that of nitroarenes using saturated alcohols.[6] These methods provided a variety of methods for synthesizing quinoline derivatives.

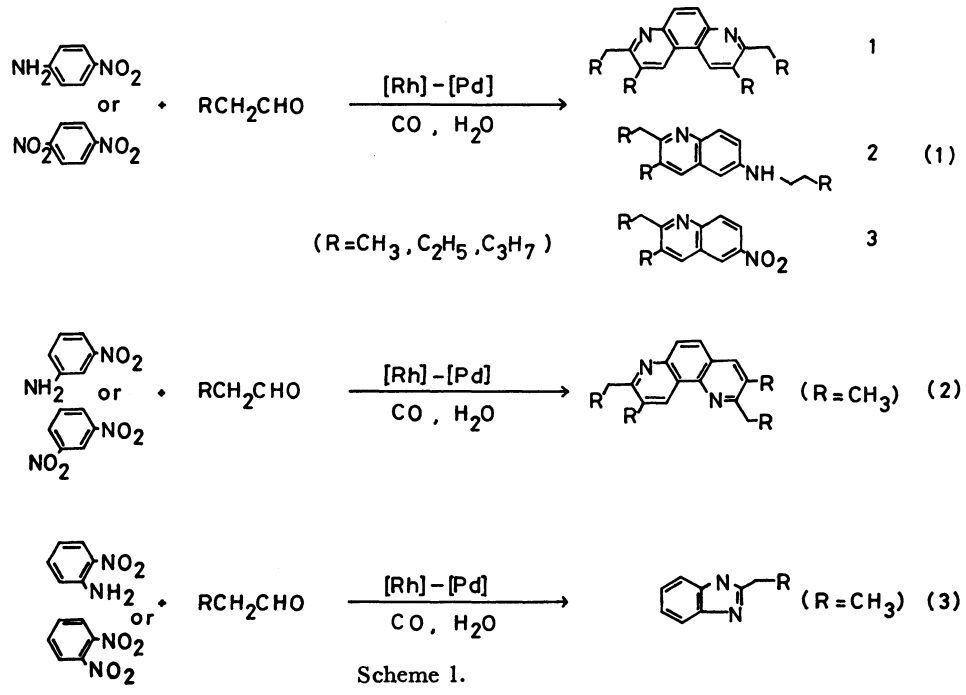
In this paper, phenanthroline derivatives were prepared by the double *N*-heterocyclization of nitroanilines and dinitrobenzenes using n-C_3—C_5 aliphatic aldehydes in the presence of a binary catalyst system ($RhCl(PPh_3)_3$–$PdCl_2$) under the pressure of carbon monoxide.

1,7-Phenanthroline and imidazole derivatives were also obtained by the reaction of *m*-nitroaniline and *o*-nitroaniline respectively with propanal.

Results and Discussion

At the outset, *p*-nitroaniline was allowed to react with propanal at 180 °C in the presence of a rhodium and/or palladium complex under carbon-monoxide pressure. In this reaction, 3,8-diethyl-2,9-dimethyl-4,7-phenanthroline (**1**), 2-ethyl-3-methyl-6-(propylamino)quinoline (**2**), and 2-ethyl-3-methyl-6-nitroquinoline (**3**) were obtained as the products (Eq. 1). This reaction was examined in detail in order to determine the optimum conditions for the preparation of **1**.

A variety of rhodium and/or palladium complexes



Scheme 1.

TABLE 1. *N*-HETEROCYCLIZATION OF *p*-NITROANILINE WITH PROPANAL USING RHODIUM AND/OR PALLADIUM COMPLEXES AS CATALYSTS[a)]

Run No.	Rh and/or Pd complexes		Conversion[b)] %	Product yield %[b,c)] 1	2	3
1	$RhCl(PPh_3)_3$	(0.17 mmol)	100	43	19	4
	$PdCl_2$	(0.26 mmol)				
2	$RhCl_3 \cdot 3H_2O$	(0.17 mmol)	100	46	15	5
	$Pd(PPh_3)_4$	(0.26 mmol)				
3	$RhCl_3 \cdot 3H_2O$	(0.17 mmol)	100	44	27	3
	$PdCl_2$	(0.26 mmol)				
	PPh_3	(0.26 mmol)				
4	$RhCl_3 \cdot 3H_2O$	(0.17 mmol)	100	30	18	0
	$PdCl_2$	(0.26 mmol)				
5	$RhCl(PPh_3)_3$	(0.17 mmol)	99	11	2	0
	$PdCl_2$	(0.26 mmol)				
	PPh_3	(0.26 mmol)				
6	$RhCl_3 \cdot 3H_2O$	(0.17 mmol)	100	25	19	0
7	$RhCl_3 \cdot 3H_2O$	(0.43 mmol)	100	31	13	0
8	$RhCl(PPh_3)_3$	(0.17 mmol)	95	5	10	0
9	$[RhCl(COD)]_2$	(0.17 mmol)	100	3	14	2
10	$Rh_4(CO)_{12}$	(0.17 mmol)	100	3	3	3
11	$PdCl_2$	(0.43 mmol)	99	23	10	12
12	$Pd(PPh_3)_4$	(0.26 mmol)	90	4	1	1

a) A mixture of *p*-nitroaniline (20 mmol), propanal (90 mmol), water (2 ml), a rhodium and/or palladium complex, and ethanol (20 ml) was heated at 180 °C under the pressure of carbon monoxide (70 atm) for 4 h. b) Based on the amount of *p*-nitroaniline used. Determined by GLC. c) **1**: 3,8-Diethyl-2,9-dimethyl-4,7-phenanthroline, **2**: 2-ethyl-3-methyl-6-(propylamino) quinoline, **3**: 2-ethyl-3-methyl-6-nitroquinoline.

was examined as catalysts, the results are shown in Table 1. In these runs, the conversion of nitroaniline was high. In some cases, a tarry material was also formed.

The yields of the products depended greatly on the catalysts used. A binary catalyst system was effective for the double *N*-heterocyclization to give **1** in 43—46% yields (Runs 1, 2, and 3). The catalyst systems, such as $RhCl(PPh_3)_3$–$PdCl_2$ (Run 1), $RhCl_3$–$Pd(PPh_3)_4$ (Run 2), and $RhCl_3$–$PdCl_2$–PPh_3 (Run 3), gave almost the same yield of **1**. The presence of triphenylphosphines enhanced the yield of **1** (Runs 3 and 4), although the addition of triphenylphosphine to the combination of $RhCl(PPh_3)_3$–$PdCl_2$ retarded the formation of **1** (Run 5). On the other hand, when a rhodium catalyst was used alone, the yield of **1** decreased considerably. In those cases, $RhCl_3$–$3H_2O$ was effective for the formation of **1** (Run 6), followed by μ,μ'-dichlorobis(cyclooctadiene)dirhodium ($[RhCl(COD)]_2$) (Run 9), $Rh_4(CO)_{12}$ (Run 10), and $RhCl(PPh_3)_3$ (Run 8). An increase in the amount of the $RhCl_3 \cdot 3H_2O$, however, resulted in only a small increase in the yield of **1** (Runs 6 and 7). Palladium complexes alone, such as $PdCl_2$ and $Pd(PPh_3)_4$, also showed catalytic activities, but with low yields of **1** (Runs 11 and 12).

Next, the effects of other reaction variables were examined. The results are listed in Table 2. A binary system, $RhCl(PPh_3)_3$ (0.17 mmol) and $PdCl_2$ (0.26 mmol), was used as the catalyst. A four-fold molar quantity of propanal (80 mmol) is required for the double *N*-heterocyclization of nitroanilines (20 mmol) stoichiometrically. A moderate yield of **1** (43%) was obtained when 90 mmol of the aldehyde was used. An increase in the amount of the aldehyde to 120 or 160 mmol, however, resulted in a decrease in the yields of **1**, **2**, and **3** and an increase in the amouns of tarry materials. An aldol condensation may interfere with the reaction in these cases (Runs 13 and 14). Concerning the reaction temperature, an elevated temperature (180 °C) was needed for the reaction. Lower and higher temperatures gave poorer yields of **1** (Runs 15 and 16). Prolonging the reaction time from 4 h to 8 h slightly improved the yield of **1** and **2** (Run 18). Even a 2 h reaction time almost completed the reaction (Run 17). Among the solvents examined, ethanol was the best, followed by methanol, benzene, and tetrahydrofuran

TABLE 2. EFFECTS OF REACTION VARIABLES ON PRODUCTS DISTRIBUTION[a)]

Run No.	Propanal (mmol)	Reaction temp/°C	Reaction time/h	Solvent	Conversion[b)] %	Product yield/%[b,c)] 1	2	3
1	90	180	4	EtOH	100	43	19	4
13	120	180	4	EtOH	98	26	10	3
14	160	180	4	EtOH	94	20	7	0
15	90	150	4	EtOH	96	12	6	1
16	90	200	4	EtOH	100	38	23	3
17	90	180	2	EtOH	100	39	21	1
18	90	180	8	EtOH	100	46	24	4
19	90	180	4	EtOH[d)]	98	7	3	2
20	90	180	4	MeOH	98	35	17	1
21	90	180	4	THF	100	24	9	2
22	90	180	4	Benzene	95	26	17	4
23[e)]	90	180	4	EtOH	100	11	15	8

a) A mixture of *p*-nitroaniline (20 mmol), propanal (90—160 mmol), water (2 ml), $RhCl(PPh_3)_3$ (0.17 mmol), $PdCl_2$ (0.26 mmol), and a solvent (20 ml) was treated at 150—200 °C under the pressure of carbon monoxide (70 atm) for 2—8 h. b) Based on the amount of *p*-nitroaniline used. Determined by GLC. c) **1**: 3,8-Diethyl-2,9-dimethyl-4,7-phenanthroline, **2**: 2-ethyl-3-methyl-6-(propylamino)-quinoline, **3**: 2-ethyl-3-methyl-6-nitroquinoline. d) Without water. e) Under the pressure of hydrogen (70 atm) instead of carbon monoxide.

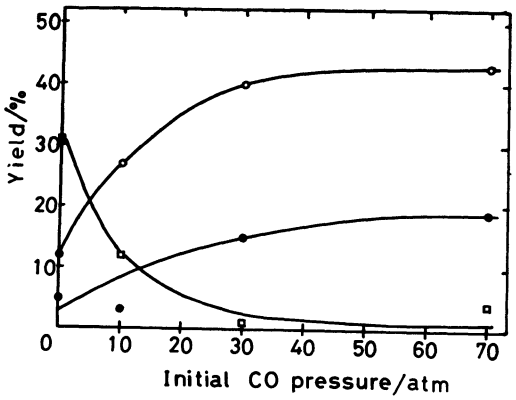


Fig. 1. Effects of pressure of carbon monoxide on products distribution.
A mixture of *p*-nitroaniline (20 mmol), propanal (90 mmol), water (2 ml), $RhCl(PPh_3)_3$ (0.17 mmol), $PdCl_2$ (0.26 mmol), and ethanol (20 ml) was treated at 180 °C for 4 h. Yields were based on an amount of *p*-nitroaniline used and determined by GLC. ○: 3,8-Diethyl-2,9-dimethyl-4,7-phenanthroline, ●: 2-ethyl-3-methyl-6-(propylamino)quinoline, □: 2-ethyl-3-methyl-6-nitroquinoline.

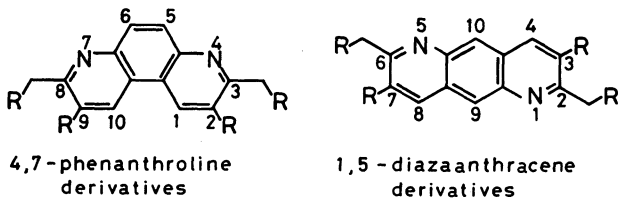
(Runs 1, 20, 21, and 22). The yields of **1** and **2** decreased considerably when the reaction was carried out without water (Run 19). Thus, water is indispensable for the reductive *N*-heterocyclization of nitroarene under carbon-monoxide pressure. Furthermore, under hydrogen pressure (70 atm) instead of carbon monoxide, **1** was also produced, but in only low yield (Run 23). These results indicated that the water-gas-shift reaction was operative for the reaction.

The relation between the initial pressure of carbon monoxide and the yield of the products is shown in Fig. 1. Under an argon atmosphere ($P_{CO}=0$), **3** was a dominant product in a yield of more than 30%, while **1** and **2** were given as minor products, indicating that carbon-monoxide pressure is not necessary for the *N*-heterocyclization of the aminoarene moiety, as was shown in previous paper.[3] However, with increases in the pressures of carbon monoxide to 10—70 atm, the yields of **3** decreased and then **1** and **2** became the major products, with a reduction of the nitroarene moiety. A pressure of carbon monoxide higher than 30 atm is required for the major production of **1**.

By inference from the result of the *N*-heterocyclization of aminoarene,[3] we first expected *p*-phenylenediamine to be a suitable substrate for the double *N*-heterocyclization. However, that is not the case. A mixture of *p*-phenylenediamine (20 mmol), $[RhCl(NBD)]_2$ (0.17 mmol), which was an excellent catalyst for the formation of quinoline derivatives from aminoarene and aldehyde,[3] propanal (90 mmol), ethanol (20 ml), and *p*-nitroaniline (30 mmol) or nitrobenzene (60 mmol) as oxidizing agents was heated at 180 °C under an argon atmosphere for 4 h. The yields of **1** were only 1—2%, based on the *p*-phenylenediamine used. In this case, one amino group may interfere with the *N*-heterocyclization of the other amino group in the same molecule.

This procedure can be applied to a variety of other aliphatic aldehydes and nitroarenes for the preparation of phenanthroline derivatives. The results are summarized in Table 3. *p*-Nitroaniline reacted with propanal, butanal, and pentanal to give the corresponding phenanthroline derivatives in fairly good yields of 43, 57, and 54% respectively (Runs 1, 24, and 25). The conbination of *p*-nitroaniline and ethanal, however failed to give the product, and a tarry material was formed. As the substrate, *p*-dinitrobenzene can be employed in this reaction, although the yield was rather low (Run 26).

As for the structure of the product mentioned above, two isomers were possible because of the two directions in the cyclization. In the reaction of *p*-nitroaniline or *p*-dinitrobenzene with the aldehyde, two isomers, 4,7-phenanthroline and 1,5-diazaanthracene derivatives, were possible (Scheme 2). The absence of J_{C-C-H} in the non-decoupling ^{13}C-NMR spectra clearly indicated that the products are not 1,5-diazaanthracene, but 4,7-phenanthroline derivatives, as is shown in Eq. 1. In the non-decoupling ^{13}C-NMR spectrum of the product, one of the aromatic carbon resonances, with a shoter T_1, appeared as a doublet ($J_{C-H}=163$ Hz) without any further long-range coupling. The resonance is assigned



Scheme 2.

Table 3. Synthesis of phenanthroline derivatives from nitroarenes and aldehydes[a]

Run No.	Nitroarene	Aldehyde	Product	Yield/%[b]
1	*p*-Nitroaniline	Propanal	3,8-Diethyl-2,9-dimethyl-4,7-phenanthroline	43 (26)
24	*p*-Nitroaniline	Butanal	2,9-Diethyl-3,8-dipropyl-4,7-phenanthroline	57 (13)
25	*p*-Nitroaniline	Pentanal	3,8-Dibutyl-2,9-dipropyl-4,7-phenanthroline	54 (33)
26	*p*-Dinitrobenzene	Propanal	3,8-Diethyl-2,9-dimethyl-4,7-phenanthroline	14
27	*m*-Nitroaniline	Propanal	2,8-Diethyl-3,9-dimethyl-1,7-phenanthroline	21
28	*m*-Dinitrobenzene	Propanal	2,8-Diethyl-3,9-dimethyl-1,7-phenanthroline	15
29	*o*-Nitroaniline	Propanal	2-Ethylbenzimidazole	24
30	*o*-Dinitrobenzene	Propanal	2-Ethylbenzimidazole	10

a) A mixture of nitroarene (20 mmol), aldehyde (90 mmol), water (2 ml), $RhCl(PPh_3)_3$ (0.17 mmol), $PdCl_2$ (0.26 mmol), and ethanol (20 ml) was treated at 180 °C under the pressure of carbon monoxide (70 atm) for 4 h. b) GLC yield based on the amount of nitroarene used. Parentheses indicate isolated yields.

to C_5 (or C_6) of 4,7-phenanthroline derivatives, since $J_{C_5-C-C-H_1}$ is too small and since the C_5 (or C_6) carbon resonance does not show any long-range coupling in the spectra. If the product is the 1,5-diazaanthracene derivative, all the resonances of the aromatic carbon resonances having shorter T_1 values will appear as peaks with a long-range coupling of 4—5 Hz ($J_{C_9-C-H_8}$, $J_{C_8-C-H_9}$). The absence of such a long-range coupling clearly indicated the product was 4,7-phenanthroline derivative.

Subsequently this reaction is applied to other nitroaniline and dinitrobenzene isomers. In the reaction with propanal, *m*-nitroaniline and *m*-dinitrobenzene gave 1,7-phenanthroline derivative in yields of 21 and 15% respectively (Runs 27 and 28) (Eq. 2). In this case, there are also two possible structures of the product based on a direction of the cyclization. However, in this case two nonequivalent peaks of methyl and ethyl groups appeared in the ^1H and ^{13}C-NMR spectra. This fact clearly indicated that the product was a 1,7-phenanthroline derivative, not a synmetric 1,8-diazaanthracene derivative.

o-Nitroaniline and *o*-dinitrobenzene failed to give a 1,10-phenanthroline derivative, but 2-ethylbenzimidazole was produced in poor yields (Runs 29 and 30) (Eq. 3).

The mechanism of the binary catalyst system is not yet clear, but several palladium complexes have been reported to form a ortho-metalated complex easily.[7] We previously suggested that the ortho-metalated species was a key intermediate in the rhodium complex-catalyzed *N*-heterocyclization of aminoarenes with aldehydes.[3] In the present reaction, palladium complex might be operative in the ortho-metalated step in the catalytic cycle. However, another factor, the so-called synergism, might also work in the reaction.

Experimental

The melting points and boiling points are uncorrected. The melting points were taken on a Yanagimoto capillary melting-point apparatus. The IR spectra were measured on a Hitachi model 215 grating spectrophotometer. The ^1H-NMR-spectra were obtained at 60 MHz with a JEOL JNM-PMX 60 spectrometer or at 220 MHz with a Varian Model HR-220 spectrometer. ^{13}C NMR spectra were measured at 25.05 MHz with a JEOL JNM FX 100. Samples were dissolved in $CDCl_3$, and the chemical-shift values were expressed in δ relative to Me_4Si as the internal standerd. Elemental analyses were performed at the Microanalytical Center of Kyoto University. The mass spectra were recorded on a JMS OlSG mass spectrometer.

The aldehydes, the nitroarenes, and the other materials employed in this study were commercial products. The aldehydes were distilled before use. Carbon monoxide was used without further purification. Anhydrous ethanol was dried by the usual method with Mg.

A 100 ml stainless steel autoclave equipped with a magnetic stirrer was used. The general experimental procedure is exemplified by the reaction of *p*-nitroaniline with propanal. A mixture of *p*-nitroaniline (2.76 g, 20 mmol), propanal (5.23 g, 90 mmol), water (2.0 ml), $RhCl(PPh_3)_3$ (0.17 mmol), $PdCl_2$ (0.26 mmol), and anhydrous ethanol (20 ml) was stirred at 180 °C under carbon monoxide (initial pressure, 70 atm at room temperature).

The autoclave was heated to 180 °C (20 min required) and then held at this temperature for 4 h. After cooling, the autoclave was discharged and the ethanol was evaporated from the reaction mixture under a vacuum. The GLC analysis of the reaction product was made using an internal standard (*N,N*-dibenzylaniline): A column (0.3 cmϕ × 3 m) packed with 5% Silicone GE SE-30 on Shimalite W 60—80 mesh. The reaction products were then subjected to fractional distillation or column chromatography (silica gel, $CHCl_3$). Recrystallization was done by means of ether. The identity of the compound was comfirmed by IR, ^1H-NMR, ^{13}C-NMR, mass spectra, and elemental analysis.

The analytical data of the phenanthroline derivatives and other products obtained here may be described as follows:

3,8-Diethyl-2,9-dimethyl-4,7-phenanthroline. Yellow crystals, mp 133—136 °C. ^1H-NMR (220 MHz) ($CDCl_3$): δ 1.39 (t, 6H, $2CH_3$), 2.55 (s, 6H, $2CH_3$), 3.01 (q, 4H, $2CH_2$), 8.08 (s, 2H), 8.46 (s, 2H). ^{13}C-NMR (25.05 MHz) ($CDCl_3$): δ 12.8 (q, $2CH_3$), 19.3 (q, $2CH_3$), 29.2 (t, $2CH_2$), 122.7 (s), 129.3 (s), 130.3 (d), 130.7 (d), 145.5 (s), 162.3 (s). MS: *m/e* 264 (M^+). Found: C, 80.79; H, 7.60; N, 10.49%. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60%.

2,9-Diethyl-3,8-dipropyl-4,7-phenanthroline. Yellow crystals, mp 77—79 °C. ^1H-NMR (220 MHz) ($CDCl_3$): δ 1.09 (t, 6H, $2CH_3$), 1.41 (t, 6H, $2CH_3$), 1.87 (sex, 4H, $2CH_2$), 2.95 (q, 4H, $2CH_2$), 2.96 (t, 4H, $2CH_2$), 8.09 (s, 2H), 8.58 (s, 2H). ^{13}C-NMR (25.05 MHz) ($CDCl_3$): δ 14.4 (q, $2CH_3$), 15.1 (q, $2CH_3$), 23.0 (t, $2CH_2$), 25.7 (t, $2CH_2$), 37.5 (t, $2CH_2$), 122.9 (s), 129.1 (d), 130.5 (d), 135.5 (s), 145.4 (s), 161.1 (s). Found C, 82.52; H, 9.00; N, 8.66%. Calcd for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74%.

3,8-Dibutyl-2,9-dipropyl-4,7-phenanthroline. Yellow crystals, mp 79—81 °C. ^1H-NMR (220 MHz) ($CDCl_3$): δ 0.99 (t, 6H, $2CH_3$), 1.09 (t, 6H, $2CH_3$), 1.51 (sex, 4H, $2CH_2$), 1.46—1.56 (m, 8H, $4CH_2$), 2.87 (t, 4H, $2CH_2$), 3.02 (t, 4H, $2CH_2$), 8.08 (s, 2H), 8.54 (s, 2H). ^{13}C-NMR (25.05 MHz) ($CDCl_3$): δ 14.1 (q, $2CH_3$), 14.2 (q, $2CH_3$), 23.0 (t, $2CH_2$), 24.2 (t, $2CH_2$), 32.0 (t, $2CH_2$), 34.9 (t, $2CH_2$), 35.3 (t, $2CH_2$), 122.8 (s), 130.0 (d), 130.4 (d), 134.0 (s), 145.4 (s), 161.4 (s). Found: C, 83.01; H, 9.91; N, 7.32%. Calcd for $C_{26}H_{36}N_2$: C, 82.93; H, 9.64; N, 7.44%.

2,8-Diethyl-3,9-dimethyl-1,7-phenanthroline. Yellow crystals, mp 101—104 °C. ^1H-NMR (220 MHz) ($CDCl_3$): δ 1.40 (t, 3H, CH_3), 1.48 (t, 3H, CH_3), 2.48 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.02 (q, 2H, CH_2), 3.05 (q, 2H, CH_2), 7.74 (d, 1H), 7.83 (s, 1H), 7.93 (d, 1H), 9.24 (s, 1H). ^{13}C-NMR (25.05 MHz) ($CDCl_3$): δ 12.3 (q, CH_3), 13.0 (q, CH_3), 18.9 (q, CH_3), 19.2 (q, CH_3), 29.1 (t, CH_2), 29.3 (t, CH_2), 124.2 (s), 125.3 (s), 127.1 (d), 127.3 (d), 129.6 (s), 129.8 (s), 132.8 (d), 135.7 (d), 143.2 (s), 147.0 (s), 161.5 (s), 163.0 (s). Found: C, 80.49; H, 7.74; N, 10.53%. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60%.

2-Ethylbenzimidazole. White crystals, mp 175—177 °C. ^1H-NMR (220 MHz) ($CDCl_3$): δ 1.42 (t, 3H, CH_3), 3.00 (q, 2H, CH_2), 7.17—7.21 (m, 2H), 7.53—7.57 (m, 2H), 9.29 (s, 1H, N–H). ^{13}C-NMR (25.05 MHz) ($CDCl_3$): δ 12.6 (q, CH_3), 22.6 (t, CH_2), 114.5 (d), 122.0 (d), 138.6 (s), 156.8 (s). Found: C, 74.08; H, 6.77; N, 19.38%. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16%.

2-Ethyl-3-methyl-6-nitroquinoline. Yellow crystals, mp 118—120 °C. IR (KBr): 1340, 1520 cm^{-1}. ^1H-NMR (220 MHz) ($CDCl_3$): δ 1.41 (t, 3H, CH_3), 2.53 (s, 3H, CH_3), 3.03 (q, 2H, CH_2), 7.97 (s, 1H), 8.09 (d, 1H), 8.34 (d, 1H), 8.63 (s, 1H). ^{13}C-NMR (25.05 MHz) ($CDCl_3$): δ 12.2 (q, CH_3), 19.1 (q, CH_3), 29.6 (t, CH_2). MS (*m/e*): 216 (M^+). Found: C, 67.61; H, 5.48; N, 11.78%. Calcd for $C_{12}H_{12}N_2O_2$: C,

66.65; H, 5.59; N, 12.96%.

2-Ethyl-3-methyl-6-(propylamino) quinoline: Yellow crystals. IR (KBr): 3300 cm^{-1}. ^{1}H-NMR (220 MHz) ($CDCl_3$): δ 0.89 (t, 3H, CH_3), 1.19 (t, 3H, CH_3), 1.55 (sex, 2H, CH_2), 2.30 (s, 3H, CH_3), 2.84 (q, 2H, CH_2), 3.05 (t, 2H, CH_2), 3.73 (s, 1H, N–H), 6.50—7.73 (m, 4H).

This work was supported by a Grant-in-Aid, Ministry of Education, Science and Culture, Japan (No. 56550587).

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