The Transition Metal-catalyzed *N*-Alkylation and *N*-Heterocyclization. A Reductive Transformation of Nitroarenes into (Dialkylamino)-arenes and 2,3-Dialkyl-substituted Quinolines Using Aliphatic Aldehydes under Carbon Monoxide

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The catalytic *N*-alkylation and *N*-heterocyclization of nitroarenes occur at 180 °C under a carbon monoxide pressure of 70 atm and in the presence of aldehyde and such transitionmetal complexes as rhodium and palladium complexes, thus giving 2,3-dialkyl-substituted quinolines and (dialkylamino)arenes in good yields. The product selectivity depends greatly on the catalysts: a binary catalyst, $RhCl(PPh_3)_3$ and $PdCl_2$, is effective for the *N*-heterocyclization, while $[Rh_2Cl_2(cod)_2]$ is effective for the *N*-alkylation.

The reduction of nitroarenes by carbon monoxide using rhodium, palladium, and selenium compounds as catalysts has been of much interest recently.[1] Nitroarenes can be converted into a wide variety of useful *N*-containing compounds, such as aminoarenes,[1a] diarylureas,[1b] aryl isocyanates,[1c] alkyl carbanilates,[1d] and *N*-arylbenzamides.[1e]

On the other hand, during the course of our study of the rhodium-catalyzed *N*-alkylation of amines by means of a carbon monoxide–water system,[2] we found that a rhodium complex is an efficient catalyst for the *N*-heterocyclization, the preparation of quinolines from aminoarenes and aliphatic aldehydes under non-acidic conditions.[3]

Ortho-substituted nitroarenes such as *o*-nitrocinnamaldehyde can also be converted into quinolines by means of an intramolecular cyclization using tetracarbonylferrate(0).[4]

More recently, we also found that nitrobenzene was selectively transformed into substituted quinolines and *N*,*N*-dialkylanilines by the rhodium- and/or palladium-catalyzed reduction with carbon monoxide in the presence of an aldehyde.[5]

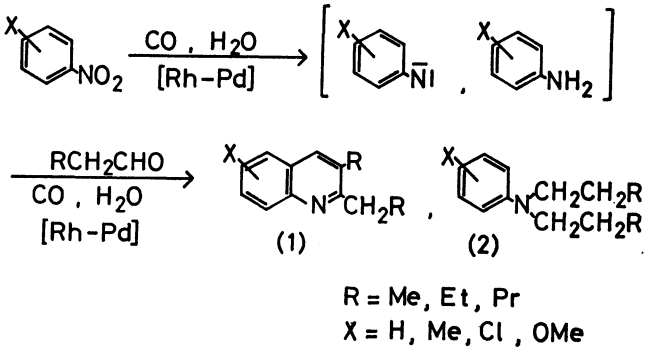
In this paper a detailed study of the reductive transformation of nitroarenes catalyzed by transition-metal complexes to quinolines and aminoarenes will be described.

Results and Discussion

Effects of Rhodium Complexes as Catalysts. Nitrobenzene combined with butanal in this procedure gave 3-ethyl-2-propylquinoline (**1**) or *N*,*N*-dibutylaniline (**2**). This combination for the preparation of **1** and **2** was examined in some detail in order to determine the optimum conditions for *N*-heterocyclization and *N*-alkylation.

A variety of rhodium complexes was examined as catalysts; the results are shown in Table 1.

The products depended greatly on the catalysts. Chlorotris(triphenylphosphine)rhodium(I), (carbonyl)-(hydrido)tris(triphenylphosphine)rhodium(I), and (carbonyl)chlorobis (triphenylphosphine)rhodium(I) gave **1** exclusively, while di-μ-chloro-bis[(cyclooctadiene)rhodium(I)], $[Rh_2Cl_2(cod)_2]$, di-μ-chloro-bis[(norbornadiene)rhodium(I)], $[Rh_2Cl_2(nbd)_2]$, dodeca(carbonyl) tetrarhodium(0), and tetra(carbonyl)dichlorodirhodium(I) favored the formation of **2**. Rhodium(III) chloride and hexadeca(carbonyl)hexarhodium(0) gave a mixture of **1** and **2**. The yields of **2** were improved by prolonging the reaction time to 8 h, while the yields of **1** were not. Only trace amounts *N*-butylaniline and aniline were detected as by-products. The reac-



Scheme 1.

TABLE 1. EFFECTS OF RHODIUM COMPLEXES AS CATALYSTS[a]

Run No.	Rh complexes[b]	Conversion[c] %	Product yield %[c,d] 1	2
1	$RhCl(PPh_3)_3$	51	11	0
2	$RhH(CO)(PPh_3)_3$	50	11	0
3	$RhCl(CO)(PPh_3)_2$	44	10	0
4	$[Rh_2Cl_2(cod)_2]$	37	0	28
5	$[Rh_2Cl_2(nbd)_2]$	43	0	34
6	$[Rh_2Cl_2(nbd)_2]$[e]	64	0	47
7	$Rh_4(CO)_{12}$	65	0	27
8	$[Rh_2Cl_2(CO)_4]$	38	0	23
9	$RhCl_3 \cdot 3H_2O$	55	7	28
10	$RhCl_3Py_3$	47	6	13
11	$Rh_6(CO)_{16}$	100	3	15

a) A mixture of nitrobenzene (40 mmol), butanal (90 mmol), water (2 ml), rhodium complex (0.09 mmol), and ethanol (20 ml) was treated at 180 °C under pressures of carbon monoxide (70 atm) for 4 h. b) [Rh] = 0.09 mmol c) Based on the amount of nitrobenzene used. Determined by GLC. d) **1**: 3-Ethyl-2-propylquinoline, **2**: *N*,*N*-dibutylaniline. e) The reaction time, 8 h.

tion by the use of $RhCl(PPh_3)_3$ gave a poor yield and selectivity of **1**. We can suggest two reasons for this. One is that butanal might be reduced to alcohol or suffer condensation to give the unreactive high-molecular-weight species by self-condensation or reaction with nitrobenzene. The other is that nitrobenzene might be reduced and transformed into urea or carbamate.[1] This situation is not yet clear.

Effects of Phosphine and Phosphite Ligands. The product selectivity of the rhodium catalysts appears to be highly affected by the triphenylphosphine coordination. The rhodium complexes with triphenylphosphine as a ligand are favorable for **1**, while $[Rh_2Cl_2(cod)_2]$ is favorable for **2**. Therefore, a combination of several phosphines and phosphite with $[Rh_2Cl_2(cod)_2]$ was tested in the reaction. The results are summarized in Table 2.

When 3 molar equivalents of triphenylphosphine, bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, and 1,3-bis(diphenylphosphino)propane were added to $[Rh_2Cl_2(cod)_2]$, the product selectivity was dramatically changed to **1** from **2**. However, in the case of triphenyl phosphite, trimethyl phosphite, and triethyl phosphite, the product selectivity was not changed. Tributylphosphine combined with $[Rh_2Cl_2(cod)_2]$ showed a unique reactivity. The conversion of nitrobenzene was very high, and *N*-(2-ethylhexylidene)aniline (**3**) was isolated in a 36% yield.

Table 2. Effects of phosphine and phosphite ligands[a]

Run No.	Ligands	Conversion[b] %	Product yield/%[b,c] 1	2
4		37	0	28
12	PPh_3	31	10	0
13	$Ph_2PCH_2PPh_2$	82	10	0
14	$Ph_2P(CH_2)_2PPh_2$	52	12	0
15	$Ph_2P(CH_2)_3PPh_2$	51	12	0
16	$P(OPh)_3$	40	0	24
17	$P(OCH_3)_3$	31	0	20
18	$P(OCH_2CH_3)_3$	35	0	24
19	$P(CH_2CH_2CH_2CH_3)_3$[d]	86	9	0

a) A mixture of nitrobenzene (40 mmol), butanal (90 mmol), water (2 ml), $[Rh_2Cl_2(cod)_2]$ (0.09 mmol), phosphine or phosphite (P/Rh=3), and ethanol (20 ml) was treated at 180 °C under pressures of carbon monoxide (70 atm) for 4 h. b) Based on the amount of nitrobenzene used. Determined by GLC. c) **1**: 3-Ethyl-2-propylquinoline, **2**: *N,N*-dibutylaniline. d) *N*-(2-Ethylhexylidene)aniline (**3**) was isolated in a 36% yield.

Effects of a Binary Catalyst. A binary catalyst, $RhCl(PPh_3)_3$ and palladium(II) chloride, $PdCl_2$, was examined for the preparation of **1**. Several reports have demonstrated that palladium complexes are effective for the reduction of nitrobenzene.[6] Some typical results are listed in Table 3.

The catalytic activity and product selectivity were highly improved by using the binary catalyst. The combination of 0.17 mmol of $RhCl(PPh_3)_3$ and 0.26 mmol of $PdCl_2$ gave an excellent conversion and a fairly good yield of quinolines **1**. The selectivity of **1** amounted to more than 70% (Run 23). $PdCl_2(PhCN)_2$ can also be used for this reaction. On the other hand, the combination of $[Rh_2Cl_2(cod)_2]$ and $PdCl_2$ improved conversion to 100%, but gave a mixture of **1** and **2** with a poorer selectivity.

A palladium species is liable to form an ortho-metallated complex.[7] Therefore, in this study the palladium catalyst may work in activation of the ortho carbon–hydrogen bond.

The Application to a Variety of Nitroarenes and Aldehydes. This produce using butanal can be applied to a variety of nitroarenes for the preparation of 2,3-dialkyl-substituted quinolines and (dialkylamino)arenes. A binary catalyst, $RhCl(PPh_3)_3$ (0.17 mmol) and $PdCl_2$ (0.26 mmol), is effective for the formation of **1** derivatives, while $[Rh_2Cl_2(cod)_2]$ (0.17 mmol) is effective for the formation of **2** derivatives. The results of *o*- and *p*-substituted nitrobenzenes including methyl, methoxyl, and chloro groups are summarized in Tables 4 and 5.

p-Methyl- and *p*-chloronitrobenzene reacted with butanal to give the corresponding 2,3,6-trisubstituted quinolines or *N,N*-dibutylaniline derivatives in fairly good isolated yields. *p*-Nitroanisole, however, gave the products in poor yields, indicating that the methoxyl group located at the para position has an inhibitory

Table 3. The reaction by a binary catalyst[a]

Run No.	Catalyst	Conversion[b] %	Product yield/%[b,c] 1	2
1	$RhCl(PPh_3)_3$(0.09 mmol)	51	11	0
0.09 mmol/4	$[Rh_2Cl_2(cod)_2]$(0.09 mmol)	37	0	28
20	$RhCl(PPh_3)_3$(0.09 mmol), $PdCl_2$ (0.09 mmol)	67	25	0
21	$RhCl(PPh_3)_3$(0.09 mmol), $PdCl_2$ (0.26 mmol)	70	44	0
22	$RhCl(PPh_3)_3$(0.26 mmol), $PdCl_2$ (0.09 mmol)	64	39	0
23	$RhCl(PPh_3)_3$(0.17 mmol), $PdCl_2$ (0.26 mmol)	82	60	0
24	$RhCl(PPh_3)_3$(0.26 mmol), $PdCl_2$ (0.26 mmol)	91	60	0
25	$RhCl(PPh_3)_3$(0.17 mmol), $PdCl_2(PhCN)_2$(0.26mmol)	100	55	0
26	$[Rh_2Cl_2(cod)_2]$(0.17 mmol), $PdCl_2$(0.26 mmol)	100	15	46
27	$PdCl_2$(0.14 mmol)	23	10	0

a) A mixture of nitrobenzene (40 mmol), butanal (90 mmol), water (2 ml), a rhodium and/or palladium complex, and ethanol (20 ml) was treated at 180 °C under pressures of carbon monoxide (70 atm) for 4 h. b) Based on the amount of nitrobenzene used. Determined by GLC. c) **1**: 3-Ethyl-2-propylquinoline, **2**: *N,N*-dibutylaniline

TABLE 4. SYNTHESIS OF QUINOLINE DERIVATIVES FROM *o*- AND *p*-SUBSTITUTED NITROARENES AND ALDEHYDES[a)]

Run No.	Nitroarene	Aldehyde	Product	Yield/%[b)]
23	H	Butanal	3-Ethyl-2-propylquinoline	35
28	*p*-Me	Butanal	3-Ethyl-6-methyl-2-propylquinoline	31
29	*p*-Cl	Butanal	6-Chloro-3-ethyl-2-propylquinoline	44
30	*p*-MeO	Butanal	3-Ethyl-6-methoxy-2-propylquinoline	12
31	*o*-Me	Butanal	3-Ethyl-8-methyl-2-propylquinoline	33
32	*o*-Cl	Butanal	8-Chloro-3-ethyl-2-propylquinoline	29
33	*o*-MeO	Butanal	3-Ethyl-8-methoxy-2-propylquinoline	5
34	H	Propanal	2-Ethyl-3-methylquinoline	53
35	H	Pentanal	2-Butyl-3-propylquinoline	36

a) A mixture of nitroarene (40 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 pressures of carbon monoxide (70 atm) for 4 h. b) Isolated yield based on the amount of nitroarene used.

TABLE 5. SYNTHESIS OF (DIALKYLAMINO)ARENES FROM *o*- AND *p*-SUBSTITUTED NITROARENES AND ALDEHYDES[a)]

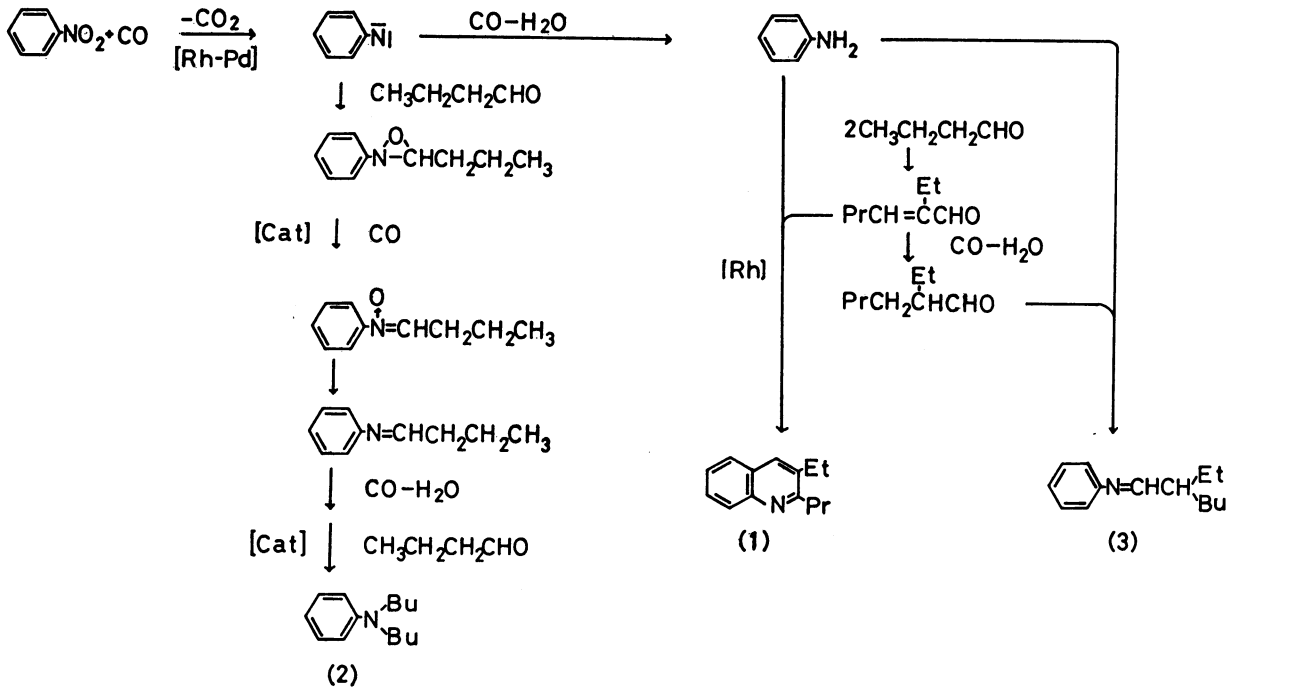
Run No.	Nitroarene	Aldehyde	Product	Yield/%[b)]
36	H	Butanal	*N*,*N*-Dibutylaniline	54
37	*p*-Me	Butanal	*N*,*N*-Dibutyl-4-methylaniline	51
38	*p*-Cl	Butanal	*N*,*N*-Dibutyl-4-chloroaniline	36
39	*p*-MeO	Butanal	*N*,*N*-Dibutyl-4-methoxyaniline	14
			N-(2-Ethylhexylidene)-4-methoxyaniline	22
40	*o*-Me	Butanal	*N*,*N*-Dibutyl-2-methylaniline	34
41	*o*-Cl	Butanal	*N*-Butyl-2-chloroaniline	33
42	*o*-MeO	Butanal	*N*,*N*-Dibutyl-2-methoxyaniline	3
			N-Butyl-2-methoxyaniline	8
43	H	Propanal	*N*,*N*-Dipropylaniline	59
44	H	Pentanal	*N*,*N*-Dipentylaniline	36
45	H	Benzaldehyde	*N*,*N*-Dibenzylaniline	3
46	H	Isobutyraldehyde	*N*,*N*-Diisobutylaniline	10

a) A mixture of nitroarene (40 mmol), aldehyde (90 mmol), water (2 ml), $[Rh_2Cl_2(cod)_2]$ (0.17 mmol), and ethanol (20 ml) was treated at 180 °C under pressures of carbon monoxide (70 atm) for 4 h. b) Isolated yield based on the amount of nitroarene used.

effect on the reaction. With *p*-nitroanisole, the *N*-(2-ethylhexylidene)aniline derivative was also given as a product. *o*-Methylnitrobenzene had a moderate reactivity to give the corresponding products. *o*-Chloronitrobenzene gave the corresponding 2,3,6-trisubstituted quinoline in moderate yields, but it gave *N*-butyl-2-chloroaniline in good yields. The reaction appeared to stop in the step of *N*-monoalkylation, so *N*,*N*-dibutyl-2-chloroaniline was not formed at all. The combination of *o*-nitroanisole with butanal almost failed to give the corresponding products.

This procedure is also applicable to a variety of aldehydes with two α-hydrogens. The combination of nitrobenzene with propanal gave 2-ethyl-3-methylquinoline and *N*,*N*-dipropylaniline in fairly good yields. Pentanal also gave 2-butyl-3-propylquinoline and *N*,*N*-dipentylaniline. In contrast to propanal, butanal, and pentanal, such aldehydes as isobutyraldehyde and benzaldehyde failed to give *N*-heterocyclization products, but did give *N*,*N*-dialkylaniline in poor yields.

Mechanism for the Reactions. The mechanism of the rhodium-catalyzed synthesis of quinolines[3)] and (dialkylamino)arenes is not yet clear. An attempt to prepare **2** directly from aniline and butanal was unsuccessful. The rhodium-, even $[Rh_2Cl_2(cod)_2]$, catalyzed reaction between aniline and butanal gives **1** in excellent yields.[3)] Thus, the formation pathways are probably different between **1** and **2**. For the formation of **1**, nitrobenzene would be reduced to aniline by the carbon monoxide–water system.[8)] The addition of aniline to the aldol condensate, α,β-unsaturated aldehyde, might occur, followed by ring closure with dehydration to form 1,2-dihydroquinoline, which would then be oxidized by nitrobenzene to form **1**. If the aldol condensates, α,β-unsaturated aldehydes, were reduced to saturated aldehyde before the Michael addition, the product **3** would be formed from aniline and the aldehyde. The fact that aldehyde with two α-hydrogens shows a great tendency toward aldol condensation under the conditions used, 200 °C in the presence of a base,[9)] suggests that α,β-unsaturated aldehyde is also one of the key intermediates in this reaction, as the case of the Doebner-von-Miller reaction.[10)] With the formation of **2**, we believe that the first step involves a catalytic deoxygenation of nitrobenzene to a nitrene, whose subsequent addition to aldehyde would give an oxaziridine and, correspondingly, an isomeric nitrone. A nitrene intermediate has been proposed for the reduction of nitrobenzene with carbon monoxide.[1)] Then, the nitrone would be reduced by carbon monoxide to a Schiff base. These steps have been proposed for the synthesis of the Schiff base from nitrobenzene.[11)] This Schiff base is



Scheme 2.

easily reduced to the secondary amine, which then reacts with one more aldehyde to form an iminium ion and finally gives **2**.

Experimental

The melting points and boiling points were 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 ^{1}H NMR spectra were obtained at 60 MHz with a JEOL JNM-60 or at 220 MHz with a Varian model HR-220 NMR spectrometer. The ^{13}C NMR spectra were determined at 25.05 MHz with a JEOL pulsed Fourier Transform spectrometer, model FX-100. Samples were dissolved in $CDCl_3$, and the chemical-shift values were expressed in δ relative to Me_4Si as the internal standard. Elemental analysis was performed at the Microanalytical Center of Kyoto University. The mass spectra were recorded on a JMS OlSG mass spectrometer.

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

An autoclave with a capacity of 100 ml, made of stainless= steel and equipped with a magnetic stirrer, was used in the reaction. A typical reaction with butanal and nitrobenzene will be described here to exemplify the general procedure adopted. A mixture of nitrobenzene (4.92 g, 40 mmol), butanal (6.49 g, 90 mmol), water (2 ml), chlorotris(triphenylphosphine)rhodium(I) (0.17 mmol), palladium(II) chloride (0.26 mmol), and anhydrous ethanol (20 ml) was stirred at 180 °C under carbon monoxide (initial pressure, 70 atm).

The autoclave was heated for 20 min to 180 °C and 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 bibenzyl as the internal standard with 10% Varsamide on Neopack 60—80 mesh (0.3 cmϕ × 3 m) The reaction products were then subjected to fractional distillation. The identity of the compound was confirmed by IR, ^{1}H NMR, ^{13}C NMR, mass spectra, and elemental analysis.

The analytical data of the quinoline derivatives gave satisfactory results.[3] The (alkylamino)- and (dialkylamino)-arenes and Schiff bases obtained here are described below. Although the products could not be isolated in an analytically pure form, they were identified on the basis of their spectral data.

3-Ethyl-2-propylquinoline (Run 23):[3] Yellow oil, bp 89—91 °C/0.24 Torr.†

N,N-*Dibutylaniline (Run 36)*: Yellow oil, bp 82—84 °C/0.23 Torr. ^{1}H NMR (220 MHz) ($CDCl_3$): δ=0.89 (t, 6H, $2CH_3$), 1.28 (sex, 4H, $2CH_2$), 1.50 (quin, 4H, $2CH_2$), 3.18 (t, 4H, $2CH_2$), 6.57—7.11 (m, 5H, Ar). Found: C, 82.03; H, 11.59; N, 6.87%. Calcd for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82%.

N-*(2-Ethylhexylidene)aniline (Run 19)*: Yellow oil, bp 78—82 °C/0.23 Torr. IR (neat) 1650, 1710, 1730 cm^{-1}. ^{1}H NMR (220 MHz) ($CDCl_3$): δ=0.86 (t, 3H, CH_3), 0.91 (t, 3H, CH_3), 1.26—1.39 (m, 4H, $2CH_2$), 1.45—1.61 (m, 4H, $2CH_2$), 2.30 (m, 1H, CH), 6.96—7.28 (m, 5H, Ar), 7.54 (d, 1H, N–CH–). ^{13}C NMR (25.05 MHz) ($CDCl_3$): δ=11.68 (q, CH_3), 14.03 (q, CH_3), 22.84 (t, CH_2), 25.36 (t, CH_2), 29.41 (t, CH_2), 31.82 (t, CH_2), 47.20 (d, CH), 120.53 (ortho), 125.22 (para), 128.86 (meta), 152.41 (arom, C-1), 170.26 (d, CH). Found: C, 80.63; H, 10.15; N, 7.02%. Calcd for $C_{14}H_{15}N$: C, 82.70; H, 10.41; N, 6.89%.

3-Ethyl-6-methyl-2-propylquinoline (Run 23):[3] Yellow oil, bp 110—114 °C/0.35 Torr.

N,N-*Dibutyl-4-methylaniline (Run 37)*: Yellow oil, bp 89—90 °C/0.28 Torr. ^{1}H NMR (220 MHz) ($CDCl_3$): δ=0.94 (t, 6H, $2CH_3$), 1.35 (sex, 4H, $2CH_2$), 1.54 (quin, 4H, $2CH_2$), 2.24 (s, 3H, CH_3), 3.23 (t, 4H, $2CH_2$), 6.56—7.24 (m, 4H, Ar).

† 1 Torr≈133.322 Pa.

6-Chloro-3-ethyl-2-propylquinoline (Run 29):[3] Yellow oil, bp 108—110 °C/0.28 Torr.

N,N-*Dibutyl-4-chloroaniline (Run 38)*: Yellow oil, bp 107—112 °C/0.28 Torr. ^{1}H NMR (220 MHz) ($CDCl_3$): δ=0.92 (t, 6H, $2CH_3$), 1.31 (sex, 4H, $2CH_2$), 1.51 (quin, 4H, $2CH_2$), 3.19 (t, 4H, $2CH_2$), 6.49—7.10 (m, 4H, Ar).

3-Ethyl-6-methoxy-2-propylquinoline (Run 30):[3] Yellow oil, bp 118—120 °C/0.28 Torr.

N,N-*Dibutyl-4-methoxyaniline (Run 39)*: Yellow oil, bp 111—114 °C/0.35 Torr. ^{1}H NMR (220 MHz) ($CDCl_3$): δ= 0.73 (t, 6H, $2CH_3$), 1.14 (sex, 4H, $2CH_2$), 1.34 (quin, 4H, Ar).

N-*(2-Ethylhexylidene)-4-methoxyaniline (Run 39)*: Yellow oil, bp 120—122 °C/0.35 Torr. IR (neat) 1650, 1700, 1730 cm^{-1}. ^{1}H NMR (220 MHz) ($CDCl_3$): δ=0.89 (t, 3H, CH_3), 0.93 (t, 3H, CH_3), 1.27—1.39 (m, 4H, $2CH_2$), 1.48—1.64 (m, 4H, $2CH_2$), 2.32 (m, 1H, CH), 3.73 (s, 3H, $-OCH_3$), 6.84—7.07 (m, 4H, Ar), 7.63 (d, 1H, N=CH–).

3-Ethyl-8-methyl-2-propylquinoline (Run 31):[3] Yellow oil, bp 105—113 °C/0.32 Torr.

N,N-*Dibutyl-2-methylaniline (Run 40)*: Yellow oil, bp 74—78 °C/0.23 Torr. ^{1}H NMR (220 MHz) ($CDCl_3$): δ=0.84 (t, 6H, $2CH_3$), 1.30 (sex, 4H, $2CH_2$), 1.41 (quin, 4H, $2CH_2$), 2.30 (s, 3H, CH_3), 2.92 (t, 4H, $2CH_2$), 6.98—7.26 (m, 4H, Ar).

8-Chloro-3-ethyl-2-propylquinoline (Run 32):[3] Yellow oil, bp 113—118 °C/0.03 Torr.

N-*Butyl-2-chloroaniline (Run 41)*: Yellow oil, bp 76—82 °C/0.50 Torr. IR (neat) 3450 cm^{-1}. ^{1}H NMR (220 MHz) ($CDCl_3$): δ=0.92 (t, 3H, CH_3), 1.41 (sex, 2H, CH_2), 1.60 (quin, 2H, CH_2), 3.09 (t, 2H, CH_2), 4.17 (s, 1H, NH), 6.61—7.27 (m, 4H, Ar).

3-Ethyl-8-methoxy-2-propylquinoline (Run 33):[3] Yellow oil, bp 116—120 °C/0.12 Torr.

2-Ethyl-3-methylquinoline (Run 34):[3] Yellow oil, bp 73—83 °C/0.57 Torr.

N,N-*Dipropylaniline (Run 43)*: Yellow oil, bp 62—66 °C/0.23 Torr. ^{1}H NMR (60 MHz) ($CDCl_3$): δ=0.88 (t, 6H, $2CH_3$), 1.57 (sex, 4H, $2CH_2$), 3.17 (t, 4H, $2CH_2$), 6.48—7.25 (m, 5H, Ar). Found: C, 81.36; H, 10.68; N, 8.00%. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90%.

2-Butyl-3-propylquinoline (Run 35):[3] Yellow oil, bp 115—118 °C/0.07 Torr.

N,N-*Dipentylaniline (Run 44)*: Yellow oil, bp 110—115 °C/0.32 Torr. ^{13}C NMR (25.05 MHz) ($CDCl_3$): δ=14.1 (q, $2CH_3$), 22.7 (t, $2CH_2$), 26.9 (t, $2CH_2$), 29.4 (t, $2CH_2$), 51.0 (t, $2CH_2$), 111.6 (ortho), 115.1 (para), 129.1 (meta), 148.1 (arom, C-1). Found: C, 82.10; H, 11.80; N, 5.88%. Calcd for $C_{16}H_{27}N$: C, 82.34; H, 11.66; N, 6.00%.

N,N-*Diisobutylaniline (Run 46)*: Yellow oil, bp 72—76 °C/0.40 Torr. ^{1}H NMR (60 MHz) ($CDCl_3$): δ=0.86 (d, 12H, $4CH_3$), 2.07 (m, 2H, 2CH), 3.10 (d, 4H, $2CH_2$), 6.57—7.30 (m, 5H, Ar).

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