differs greatly from what would be predicted (2.724 and 2.604 Å, respectively) based on the U–C and Yb–C bond distances observed in the also eight-coordinate $(CH_3C_5H_4)UCl_3(THF)_2$ and $[(CH_3C_5H_4)_2YbCl]_2$ complexes (U–C = 2.720 Å and Yb–C = 2.585 Å). It is thus clear that metal–ligand bond distances in these compounds are highly dependent on the nature and severity of interligand contacts on the coordination sphere. The metal–carbon and metal–oxygen distances in 1 and 2 seem to be much more sensitive to the presence of nonbonded contacts than do the metal–chlorine distances. The average Er–Cl bond length of 2.617 (1, 4, 4, 2) Å in 1 is quite comparable to the average U–Cl bond length of 2.623 (3, 6, 9, 3) Å in 2[15] as well as the U–Cl bond lengths of 2.599 (9, 2, 2, 2) Å in $[(C_2B_9H_{11})_2UCl_2]^{2-}$, 2.627 (2) Å in $(C_6H_5CH_2C_5H_4)_3UCl$ and 2.593 (3) Å in $(C_9H_7)_3UCl$.[35-37]

In summary, the results of this study indicate that the stereochemistry of the metal coordination sphere in monocyclopentadienyl lanthanide or actinide complexes can often be readily predicted in a strenghtforward fashion and that steric factors can have a pronounced effect on metal–ligand bond lengths in organometallic complexes of the f elements. Although little use has been made to date of the monocyclopentadienyl lanthanide or actinide complexes for more involved chemistry, there is little doubt that their easily modified coordination spheres will eventually provide a rich source of new chemistry. Finally, the possibility should be considered that related structures may well be found for large early transition-metal compounds which have the electronic capabilities to absorb the large numbers of electrons donated by such a ligand complement.[38]

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Registry No. $(C_5H_5)LnCl_2(THF)_3$, 81703-54-0.

Supplementary Material Available: Table II (a listing of calculated coordinates for the hydrogen atoms), Table IV (bond lengths and angles for nonhydrogen ligand atoms), and a table of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Rhodium and Molybdenum Complexes as Catalysts for Conversion of Nitrobenzene and Aliphatic Alcohols to Alkylquinolines

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Nitrobenzene reacts with ethanol and higher alcohols to form 2-methyl- or 2,3-dialkylquinolines, respectively. The reaction is catalyzed by rhodium or molybdenum complexes. The best yields and conversions are obtained in the presence of about equimolar mixtures of rhodium and molybdenum at ~180 °C. This latter system represents a convenient and practical synthesis of alkylquinolines. The probable reaction mechanism is discussed.

The well-known transition metal catalyzed reduction of nitrobenzene by carbon monoxide has been suggested to involve nitrene-type intermediates.[1] In order to allow the chemistry of the intermediate to be observed and prevent its trapping by carbon monoxide, we were interested in nitrobenzene deoxygenation by carbon monoxide present at low partial pressure. In this context we were intrigued by the reports[2] that a combination of group 8 metal carbonyls, such as chlorocarbonylrhodium(I) dimer (1) or tetrabutylammonium trichlorocarbonylpalladate (2), with Lewis acids, represented by molybdenum pentachloride, vanadium tri- and tetrachlorides, or titanium tetrachloride, allows reduction of nitro atomatics at ~100 kPa (1 atm) of CO and 100 °C. Interestingly, application of a similar catalyst system to reduction of nitrobenzene in alcoholic media resulted in formation of alkylquinolines instead of the expected carbamates. After our study was finished Watanabe and co-workers[3] published their account of a low-yield alkylquinoline formation from nitrobenzene and alcohols in the presence of tris(triphenylphosphine)dichlororuthenium(II). This prompted us to reveal our independent work which represents the first practical and moderate to high-yield synthesis of alkyl quinolines from nitrobenzene and extends the list of potential catalysts to rhodium and molybdenum.

Results and Discussion

Initially we examined the reduction of nitrobenzene under conditions similar to those employed by Schwetlick

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Table I. Reduction of Nitrobenzene under Carbon Monoxide at 180 °C^a

solvent	P(CO), psi	time, h	convn, %	% selectivity to quinoline	% selectivity to anilines
1-BuOH	100	22^b	97+	~80	~15
	100	2	>85	~75	
	100	2.5	>90	56^c	
1-PrOH	150	4	>95	61^c	
	150	4	50	~35^d	~35^d
	150	4	68	~85^e	
MeOH	450	2	>90	···	f
	350	2.5	94	···	trace^g

^{a} Molar ratio of $[Rh(CO)_2Cl]_2$:$MoCl_5$ = 0.5:1 unless otherwise stated. ^{b} Reaction temperature was 104 °C. ^{c} Isolated yield. ^{d} Only $[Rh(CO)_2Cl]_2$, no $MoCl_5$ was employed as the catalyst. ^{e} Only $MoCl_5$, no $[Rh(CO)_2Cl]_2$ was present. ^{f} Methyl carbanilate is the only volatile product. ^{g} <5% of methyl carbanilate was formed.

Table II. Reduction of Nitrobenzene with Alcohols under Argon at 180 °C^a

solvent	P(Ar), psi	time, h	convn, %	% selectivity to quinoline
1-BuOH	100	4.5	~100	68
1-PrOH	150	4	~100	~85
1-PrOH	150	4	100	78
1-PrOH	150	4	60^b	~70
1-PrOH	150	4	43^c	61
1-PrOH	150	4	58^d	54
EtOH	300	4	~95	~70
MeOH	450	4	100	0^e

^{a} Molar ratio of $[Rh(CO)_2Cl]_2$:$MoCl_5$ = 0.5:1 unless otherwise stated. ^{b} Only $MoCl_5$, no $[Rh(CO)_2Cl]_2$ was present. ^{c} Only $MoO_2(acac)_2$ was present. ^{d} Only $Mo(CO)_6$ was present. ^{e} Only polymeric materials were found.

et al.[2a] except that 1-butanol was substituted for *o*-dichlorobenzene and a provision was made for removal of the formed carbon dioxide. At ~100 kPa (1 atm) of CO and 100 °C, employing ~10 mol % of an equimolar mixture of chlorodicarbonylrhodium(I) dimer and molybdenum pentachloride as the catalyst, a long induction period was observed. Nonetheless, overnight about one-third of the theoretical amount of CO was consumed. Chromatographic analysis showed 48% conversion of nitrobenzene and two major products in a ratio of 1:2. These were identified as aniline and 3-ethyl-2-propylquinoline, respectively. This result suggests that reduction of nitrobenzene by both CO and butanol takes place simultaneously. The same mixture of reagents sealed in an autoclave, pressurized to 689 kPa (100 psi) with CO and heated to 180 °C yielded ca. 75% of the dialkylquinoline (by GC) at 85% conversion of nitrobenzene. Repetition of this run, followed by workup after 2.5 h of reaction, afforded 56% isolated yield of the dialkylquinoline.

Other normal alcohols, except methanol, also reacted under these conditions to give quinoline derivatives, with up to 85% (GC) selectivity in the case of 1-propanol (61% isolated yield). Methanol, on the other hand, gave only methyl phenylcarbamate as a volatile product at 3102 kPa (450 psi) of carbon monoxide pressure. At low pressures only a brown polymeric powder was obtained. The runs in the presence of CO are summarized in Table I.

In order to determine the function of carbon monoxide and alcohol in our system, nitrobenzene, $[RhCl(CO)_2]_2$, $MoCl_5$, and propanol were combined and heated at 180 °C under argon pressure for 4 h (Table II). Surprisingly, reduction of nitrobenzene was complete and 2-ethyl-3-methylquinoline was again the major product at ca. 85% selectivity. Ethanol and 1-butanol likewise afforded the corresponding quinolines in ca. 70% yield, but in methanol only the previously noted brown polymeric powder was isolated. Analysis (mass spectra) of the gas mixture from one of the runs in 1-butanol and 689 kPa (100 psi) of carbon monoxide showed only about 5% of the carbon monoxide converted to carbon dioxide as compared to 40% expected if carbon monoxide were the only reductant. These results indicate that at the reaction temperature of 180 °C and a partial pressure of carbon monoxide only slightly higher than the partial pressure of the alcohol vapors, alcohol rather than carbon monoxide becomes the predominant reducing agent.

The reaction is catalyzed by both molybdenum and rhodium complexes. With only molybdenum pentachloride as the catalyst, the reduction of nitrobenzene is much slower, although the selectivity to dialkylquinoline is still high. When only chlorodicarbonylrhodium(I) dimer is used, however, both the rate and the selectivity are much lower. The combination of the two catalysts affords the best results in terms of both rate and selectivity. The yields of quinoline products are remarkably high in these reactions, considering the numerous steps involved (Scheme I).

For catalysis by low-valent group 8 metals close analogies can be found for every step suggested in Scheme I. Palladium,[4b] rhodium,[4] and ruthenium[5] complexes catalyze dehydrogenation of alcohols to aldehydes or ketones and hydrogen transfer to different acceptors. Due to consecutive reactions, the second step, reduction of nitrobenzene to aniline by alcohols in the presence of transition-metal complexes, can be documented only indirectly. These consecutive reactions involve formation of Schiff bases from aniline and aldehydes generated in situ and their hydrogenation to *N*-alkyl- or *N*,*N*-dialkylanilines. This sequence, so far demonstrated only for ruthenium(II)-catalyzed reactions,[6] is probably valid also for rhodium(I) species. This suggestion is strongly supported by rhodium-catalyzed reduction of nitrobenzene to aniline by water and carbon monoxide[7] or by the conversion of nitrobenzene to *N*,*N*-dibutylaniline in a mixture of water, carbon monoxide, and butanol.[8] The sequence of steps 3–5 (Scheme I) is in agreement with the proposed mechanism of the acid-catalyzed Skraup's synthesis of quinolines from aldehydes and anilines.[9] In our system the function of acid

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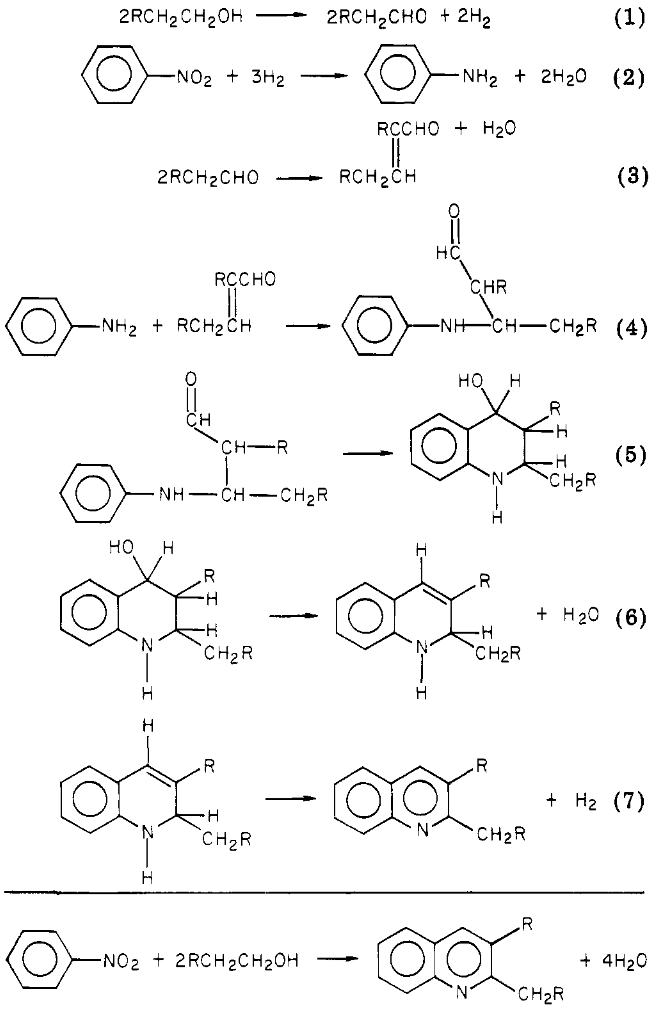
Scheme I. The Most Likely Steps in the Conversion of a Mixture of Nitrobenzene and Aliphatic Alcohols to 2,3-Dialkylquinolines



is played by transition-metal complexes (rhodium(III)). Rhodium complexes are not as efficient catalysts for the condensation steps as they are for hydrogen transfer. Accordingly, *N*-alkyl- and *N*,*N*-dialkylanilines are the major products if the reaction of nitrobenzene and alcohol is catalyzed only by rhodium (Table I) or ruthenium complexes.[3,6] The formation of alkyl- and dialylanilines can be minimized in two ways. Introduction of oxidants[10] or other hydrogen acceptors[6] will prevent hydrogenation of the intermediate Schiff bases formed from aniline and aldehydes. Employment of Lewis acids better than rhodium(III) will increase the rate of dihydroquinoline ring formation (steps 3–5 in Scheme I). In our bimetallic system, the role of the Lewis acid is played by higher valent molybdenum complexes (see below). The last step is analogous to the previously reported[4a,11] dehydrogenation of saturated heterocycles with the exception that in our system the hydrogen acceptor is nitrobenzene rather than olefins.

There is no precedent for the molybdenum-catalyzed conversion of nitrobenzene and alcohols to quinolines. Also, the support for the steps in Scheme I is not as complete as for the group 8 metal complexes. Nevertheless a few comments about the role of molybdenum in this reaction are appropriate. In contrast to group 8 metal complexes only one account has been published on hydrogen transfer catalyzed by soluble molybdenum complexes.[12] It involves hydrogen transfer to ketones from alcohols or saturated heterocycles facilitated by molybdenum(0) complexes stabilized by 1,2-bis(diphenylphosphino)ethane. Saturated heterocycles were found to be very ineffective hydrogen donors. It is very unlikely that in our system containing no stabilizing ligands, molybdenum pentachloride would be reduced to molybdenum(0).

Low-valent molybdenum species are powerful deoxygenating agents for sulfoxides and *N*-oxides.[13] Only recently, nitrobenzene was reduced to aniline by molybdenum(III) in aqueous tetrahydrofuran.[14] We have demonstrated that even bis(dithiocarbamato)oxomolybdenum(IV) deoxygenates nitrobenzene.[15] Molybdenum(VI) oxides or soluble complexes are reduced[16] in refluxing alcohol (e.g., 1-octanol) to soluble molybdenum blue species with oxidation state between 5 and 6.[17] Finally, molybdenum(V) complexes can disproportionate into tetravalent and hexavalent species.[18] Thus, it is quite feasible to visualize deoxygenation of nitrobenzene by molybdenum(IV) instead of hydrogen transfer. The generated molybdenum(VI) would be reduced by alcohol, which in turn would be oxidized to aldehydes.

High-valent molybdenum species possess strong Lewis acid properties[19] and should be good catalysts for the steps 3–5 in Scheme I. It is this quality of the higher valent molybdenum complexes, compared to their low tendency to catalyze hydrogen transfer, which assures high selectivity to dialkylquinolines and decreases the chance for hydrogenation of Schiff bases to *N*-alkyl- or *N*,*N*-dialkylanilines.

Hydrochloric acid, formed by alcoholysis of molybdenum pentachloride, does not appear to play a major role since it is neutralized by the amines as they are formed and may also react with the alcohols to form alkyl chlorides. This is further corroborated by the observation that quinolines are formed in the presence of bis(acetylacetonato)dioxomolybdenum(VI) and molybdenum hexacarbonyl (Table II). The last step, molybdenum-catalyzed dehydrogenation of a dihydroquinoline, although without a direct precedent, is reminiscent of the oxidation of alcohols by molybdenum(VI) species.

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Conclusion

Our work demonstrates that the ability to catalyze synthesis of quinolines from nitrobenzene and aliphatic alcohols is not limited to group 8 metals such as rhodium or ruthenium. On the contrary, high-valent molybdenum species proved to be even more specific catalysts than group 8 metal complexes. The best yields and reaction rates are achieved with the Mo/Rh bimetallic catalysts. In this system rhodium predominantly facilities hydrogen transfer (steps 1, 2, and 7 in the Scheme I) while molybdenum species due to their Lewis acidity catalyze mainly the condensation reaction (steps 3–6 in Scheme I).

Experimental Section

General Data. Infrared spectra, of either neat films or KBr pellets, were recorded on a Perkin-Elmer 283 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian T-60 and CFT-20 instruments, respectively. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 and retention times and peak areas monitored by a Hewlett-Packard 3352B computer. Columns employed were 1.83 m × 2 mm 3% Silar-10C on Gas-Chrom Q and 1.83 m × 2 mm 10% SE-30 on Chromsorb W-HP. GC/MS analyses were run on either a Finnegan 3300 instrument using chemical ionization or on an AEI MS902 instrument using electron impact.

Materials. Nitrobenzene was distilled from P_2O_5, stored over 4A molecular sieves, and degassed prior to use. Alcohols used were reagent grade and were dried over 4A molecular sieves and degassed before use. Chlorodicarbonylrhodium(I) dimer was obtained from Strem Chemicals, and molybdenum pentachloride, resublimed, 99+%, was purchased from Ventron and stored in a drybox. Carbon monoxide was Matheson research grade.

Nitrobenzene Reduction. All reductions were carried out in a similar manner as exemplified below.

Reduction of Nitrobenzene in Butanol under Pressure of Carbon Monoxide. In a 40-mL Parr autoclave were placed chlorodicarbonylrhodium(I) dimer (196 mg, 0.5 mmol) and biphenyl (0.606 g). The bomb was transferred to a drybox where molybdenum pentachloride (275 mg, 1 mmol) was added. The bomb was capped with a serum cap. Butanol (15 mL) was added via syringe, followed by nitrobenzene (1.17 g, 9.5 mmol). Then the bomb was sealed, under a flow of argon, cooled in dry ice, and evacuated. The bomb was warmed to room temperature and then pressurized to 690 kPa (100 psi) with carbon monoxide. It was placed in an oil bath heated to 180 °C for 2 h, then cooled, and vented. GC analysis of the reaction mixture showed >85% conversion of the nitrobenzene and three major product peaks. They were identified by GC/MS as aniline, *N*-propylaniline, and 3-ethyl-2-propylquinoline. From the relative areas of these peaks the yields of the products were estimated to be ~20%, 5%, and 75%, respectively.

Isolation of 2-Propyl-3-ethylquinoline. The autoclave was charged as before with chlorodicarbonylrhodium(I) dimer (193 mg, 0.50 mmol), molybdenum pentachloride (273 mg, 1 mmol), nitrobenzene (1.21 g, 9.8 mmol), and 1-butanol (15 mL). After being sealed, the autoclave was chilled in dry ice and evacuated. It was warmed to room temperature, pressurized with carbon monoxide (690 kPa, 100 psi), and heated in an oil bath at 180 °C for 2.5 h. The bomb was cooled and vented, and the contents were poured into 20 mL of water. The mixture was made alkaline (pH >10) to pH paper by addition of concentrated KOH solution and then extracted with ether (3 × 20 mL) with some difficulty due to emulsion formation. The combined organic layers were washed with water and saturated sodium chloride solution, then dried ($MgSO_4$), filtered, and concentrated. The residue was distilled (Kugelrohr) at 80–90 °C (0.1 mmHg) to give an oil (1.22 g). Analysis by GC and ^{1}H NMR showed the oil to be ca. 90% pure 3-ethyl-2-propylquinoline (56% yield): IR (neat film) 2980, 1620, 1500, 1430, 920, 750, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.2–7.1 (m, 5 H), 3.1–2.6 (m, 4 H), 1.85 (m, 2 H), 1.28 (t, J = 7 Hz, 3 H), 1.05 (t, J = 7 Hz, 3 H); CI-MS, *m/e* 199.

Reduction of Nitrobenzene in 1-Propanol under Argon Pressure. The 40-mL autoclave was charged as before with chlorodicarbonylrhodium(I) dimer (193 mg, 0.5 mmol), molybdenum pentachloride (273 mg, 1 mmol), biphenyl (0.651 g, 5 mmol), nitrobenzene (1.25 g, 10 mmol), and 1-propanol (15 mL), then sealed, evacuated, and pressurized with argon to 1034 kPa (150 psi). After being heated at 180 °C for 4 h, the autoclave was cooled, vented, and opened, and the liquid phase was decanted from a black solid. GC analysis of the solution showed complete conversion of the nitrobenzene and three major product peaks on either an SE-30 column or the 3% Silar 10-C column. The dominant peak was identified as 2-ethyl-3-methylquinoline by GC/MS and by coinjection with an authentic sample isolated from another run. The other two peaks were identified as aniline (GC/MS, coinjection) and *N,N*-dipropylaniline (GC/MS); there were small amounts of other products. By comparison of peak areas relative to biphenyl with those in a reference soluton prepared from aniline, 2-ethyl-3-methylquinoline, biphenyl, and 1-propanol, the yields of each product were found: ethylmethylquinoline (78%), aniline (12%), dipropylaniline (~5%).

Isolation of 2-Ethyl-3-methylquinoline. The stainless-steel autoclave was charged under argon with chlorocarbonylrhodium(I) dimer (194 mg, 0.5 mmol), molybdenum pentachloride (273 mg, 1 mmol), nitrobenzene (1.23 g, 10 mmol), and 1-propanol (15 mL). After being sealed, the autoclave was chilled in dry ice and evacuated. Upon warming to room temperature, it was pressurized with carbon monoxide to 1034 kPa (150 psi) and then heated in an oil bath at 180 °C for 4 h. After the autoclave was cooled and vented, the liquid was decanted, filtered, and concentrated on the rotary evaporator. The residue was dissolved in water (15 mL), made alkaline with KOH, and extracted with ether (4 × 15 mL); considerable difficulty with emulsions was encountered. The ether extracts were washed with water and saturated with NaCl, dried, and evaporated to give 1.29 g of orange oil. Distillation (Kugelrohr) at 65–75 °C (0.1 mm) yielded 1.13 g (61%) of yellow oil, ~90% pure by GC. This was identified by its IR, ^{1}H NMR, and chemical ionization mass spectrum as 2-ethyl-3-methylquinoline: IR (neat film) 2980, 1620, 1500, 1420, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.2–7.0 (m, 5 H), 2.9 (q, J = 7 Hz, 2 H), 2.3 (s, 3 H), 1.32 (t, J = 7 Hz, 3 H); CI-MS, *m/e* 171.

Reduction of Nitrobenzene in Methanol under Pressure of Carbon Monoxide. In the bottom part of a 40-mL stainless-steel autoclave were placed biphenyl (512 mg, 3.32 mmol) and chlorodicarbonylrhodium(I) dimer (194 mg, 0.5 mmol). The vessel was transferred to a drybox, where after addition of molybdenum pentachloride (273 mg, 1 mmol), it was stoppered with a serum cap. Degassed, dry methanol (15 mL) was added via syringe followed by degassed nitrobenzene (1.21 g, 9.8 mmol). The top of the autoclave was attached under a stream of argon. After being sealed, the autoclave was chilled in dry ice and evacuated. Upon warming to room temperature, it was pressurized to 3102 kPa (450 psi) with carbon monoxide, heated in an oil bath at 180 °C for 2 h, cooled, and vented. GC analysis of the liquid portion showed nearly complete conversion of the nitrobenzene and only one product peak. This was identified by GC/MS and by coinjection on the Silar 10-C and 10% SE-30 columns as methyl carbanilate. Approximately 0.8 g of a brown solid was isolated by filtration and appeared to be polymeric; it was insoluble in all solvents.

Reduction of Nitrobenzene in Methanol under Argon Pressure. This reaction was run exactly as the preceding one except that argon was used to pressurize the vessel to 3102 kPa (450 psi) and reaction time was 4 h. On opening the bomb a black-brown solid was obtained which is insoluble in all solvents. GC analysis of the liquid phase showed complete conversion of the nitrobenzene but no volatile products.

Registry No. Chlorodicarbonylrhodium(I) dimer, 14404-25-2; molybdenum pentachloride, 10241-05-1; 1-butanol, 71-36-3; nitrobenzene, 98-95-3; aniline, 62-53-3; *N*-propylaniline, 622-80-0; 3-ethyl-2-propylquinoline, 3290-24-2; 1-propanol, 71-23-8; 2-ethyl-3-methylquinoline, 27356-52-1; *N,N*-dipropylaniline, 2217-07-4; methanol, 67-56-1; methyl carbanilate, 2603-10-3; ethanol, 64-17-5; 2-methylquinoline, 91-63-4.