spectra were obtained on a Bruker WH-400 (^{1}H 400-MHz) spectrometer with chloroform-*d* as solvent and tetramethylsilane as an internal standard, except where otherwise indicated. ^{1}H NMR multiplicities are recorded by use of the following abbreviations: s, singlet; d, doublet; dd, doublet doublet; t, triplet; q, quartet; m, multiplet; bs, broad; *J*, coupling constant (hertz). High-resolution mass spectra were obtained by means of a Kratos MS50TCTA spectrometer at the Université de Montréal. Melting points were measured on a Büchi SMP-20 apparatus and are uncorrected. Optical rotations were measured at 589 nm on a Rudolph Research Autopol III polarimeter. The UV spectra were recorded on a Cary 1 spectrophotometer with acetonitrile as solvent at 20 °C. HPLC's were run on an Hypersil-MOS C-8 reversed-phase column (25 cm × 4.6 mm) using TFA/CH_3CN/H_2O and TFA/MeOH/H_2O as mobile phase.

General Procedure for the Condensation, Hydrolysis, and Decarboxylation. To a solution of the carboxylic acid (14.5 mmol) in tetrahydrofuran (80 mL) was added under an argon stream 1,1'-carbonyldiimidazole (2.60g, 16.05 mmol). The solution was stirred at 20 °C for 1 h and then was purged with nitrogen and cooled at −78 °C. A solution of active methylene reagent (17.4 mmol) in tetrahydrofuran (30 mL) was reacted under argon with sodium hydride (50% in mineral oil) (0.765 g, 15.9 mmol). This solution was added over a 40-min period using a syringe pump to the first solution at −78 °C. The solution was stirred at −78 °C for 1 h and was gradually warmed to 20 °C overnight. The solvent was removed, and the residue was washed vigorously with a mixture of diethyl ether/hexanes (3 × 15 mL). Formic acid (96%, 40 mL) was then added, and the solution was stirred at 20 °C for a period of 8 h followed by coevaporation of formic acid with benzene (2 × 20 mL) on a rotary evaporator. The residue was dissolved in ethyl acetate (200 mL) and washed with water (30 mL) and 5% citric acid/brine (2:1) solution (2 × 20 mL), and the aqueous phase was back-extracted with ethyl acetate/hexane (1:1) (2 × 30 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate (portions of 5–10 mL) until a neutral pH value for the aqueous layer was reached. The organic layers were washed with brine (2 × 15 mL) and dried with magnesium sulfate and then filtered on a silica gel pad (4 g) which was rinsed with ethyl acetate (30 mL). The solvent was then evaporated and the residue was recrystallized in solvents as indicated in Table II. The mother liquor was concentrated, purified by flash chromatography to afford additional portions of pure product. The products **5a–5e** were obtained as solids in 85% (**5a**), 80% (**5b**), and 75% (**5e**) yields, respectively, using *tert*-butyl cyanoacetate as the active methylene reagent. We also obtained compound **5c** in 51% yield using *tert*-butyl methyl malonate and **5d** in 83% using nitromethane (40 equiv and with sodium hydride, 12 equiv without the formic acid treatment). The physical data for products **5a–5e** are reported in Tables II and III.

General Procedure for the Silica Gel-Catalyzed Knoevenagel Condensation (Products 6a–c). The cyanomethyl ketone (1.54 mmol) and carbonyl compounds (4.6 mmol) were dissolved in dichloromethane (1.2 mL). Merck silica gel (500 mg, 230–400 mesh) was added under nitrogen. The solution was stirred at 25 °C until completion of the reaction (see reaction time in Table I) and was then filtered through a scintered glass frit prior to chromatographic purification on silica gel. Products **7–12, 18** and **19**: same procedure as above except for the ratio of reagents: silica gel (900 mg), cyanomethyl ketone (1 mmol), CH_2Cl_2 (4.5 mL), and carbonyl compound (5 mmol). Products **13–17**: same procedure as above except for the quantity of carbonyl compound used, respectively: 9, 18, 13, 9, and 18 mmol. The physical data for products **6a–6c, 7–19** are reported in Tables II and III.

HPLC Analysis of Diastereoisomers 5b and 5e. HPLC analysis with solvent A (0.1% TFA/H_2O) and solvent B (0.1% TFA/MeOH) and gradient (35% B to 60% B) in 20 min on Hypersil-MOS C-8 reversed-phase column (25 cm × 4.6 mm) at a flow rate of 1.0 mL min^{-1} indicated the presence of one isomer. For instance, injection of sample **5b** with t_{r1} 11.2 min (>99.0% optical purity) and similarly **5e** with t_{r2} 12.5 min (>99.0% optical purity).

HPLC Analysis of Diastereoisomers 18 and 19. HPLC analysis with solvent A (0.1% TFA/H_2O) and solvent B (0.1% TFA–60% CH_3CN/H_2O) and gradient (60% B to 80% B) in 15 min on Hypersil-MOS C-8 reversed-phase column (25 cm × 4.6 mm) at a flow rate of 1.0 mL min^{-1} indicated the presence of one isomer. For instance, injection of sample **18** with t_{r1} 12.8 min (>99.5% optical purity) and similarly **19** with t_{r2} 13.3 min (>99.7% optical purity).

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Supplementary Material Available: ^{1}H NMR spectra for all new compounds **5a–5e, 6a–6c**, and **7–19** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Annulation Reactions with Iron(III) Chloride: Oxidation of Imines

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Aromatic imines react with phenylacetylene or styrene in an acetonitrile solution of iron(III) chloride to give quinolines **3** or their tetrahydro derivatives **11** together with variable amounts of products **4** arising from the reduction of the imines. The initial step appears to be a one-electron oxidation to generate iron(II) and an imine radical cation. When the reactions are carried out in the presence of stoichiometric amounts of tetrachloro-*p*-benzoquinone (chloranil), only quinolines **3** are obtained.

The use of imines in constructing heterocyclic rings has been studied intensively in recent years. We have explored a series of free-radical cyclizations and annulations involving the intermediacy of imidoyl radicals generated by hydrogen abstraction from aromatic imines, by which such *N*-heterocycles as phenanthridines,[1] quinolines,[2] and

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Scheme I. Reaction of Imines 1 with Phenylacetylene and Iron(III) Chloride

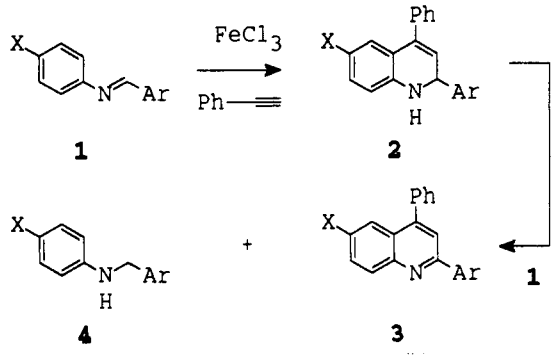


Table I. Reactions of Imines 1, Phenylacetylene, and Iron(III) Chloride[a]

imine	X	Ar	3 Yield,[b] %	4 Yield,[b] %
1a*	H	C_6H_5	46	22
1b*	MeO	C_6H_5	55	14
1c*	O_2N	C_6H_5	61	28
1a**	H	C_6H_5	76	
1b**	MeO	C_6H_5	70	
1c**	O_2N	C_6H_5	86	2
1d**	H	p-$O_2NC_6H_4$	79	
1e**	H	2-thienyl	60	
1f**	H	2-furyl	55	

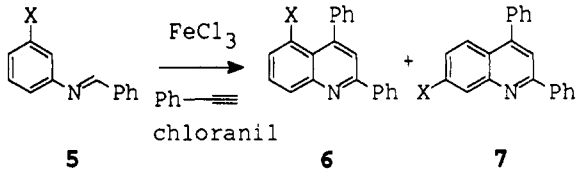
[a] Reactions indicated by an asterisk were carried out in the absence of chloranil, whereas those indicated by a double asterisk were performed with addition of chloranil; in the annulations involving imines 1a and 1d, the final reaction mixture contained *N,N'*-diarylbenzenecarboximidamide as well in about 10% yield. [b] All yields are for isolated pure products and are based on the starting imine.

benzo-1,2,4-triazines[3] are synthesized. Recently, other heterocycles have been synthesized with imidoyl radicals generated from selenoimidates.[4] The construction of quinoline derivatives has also been achieved by thermal electrocyclic rearrangement of *o*-alkenylimines.[5]

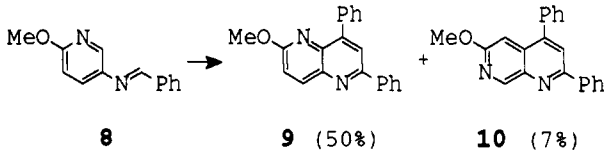
Recent investigations of electron-transfer reactions[6] and an ESR study of a series of imine radical cations[7] suggested the possibility of generating these intermediates in solution via one-electron oxidation with high-valence metal ions. Our primary target was to modify the previously reported[1,2] annulation of aromatic imines with carbon–carbon multiple bonds in order to synthesize quinoline derivatives without using a peroxide. The reported synthesis of 6-phenylphenanthridines by intramolecular ring closure of 2-(benzylideneamino)biphenyls, performed with tin(IV) chloride in high-boiling aromatic solvents, probably occurs via an imine radical cation.[8]

We here report the oxidation of a series of aromatic imines in an acetonitrile solution of iron(III) chloride, a reagent that has recently been used for the one-electron oxidation of *N,N*-dimethylaniline.[9]

Scheme II. Reaction of Imines 5 with Phenylacetylene, Iron(III) Chloride, and Chloranil



Scheme III. Reaction of Imine 8 with Phenylacetylene, Iron(III) Chloride, and Chloranil



Scheme IV. Different Products Distribution in Peroxide (ROOR) or Iron(III) Chloride Mediated Reactions of Imines 1 and 5 with Phenylacetylene

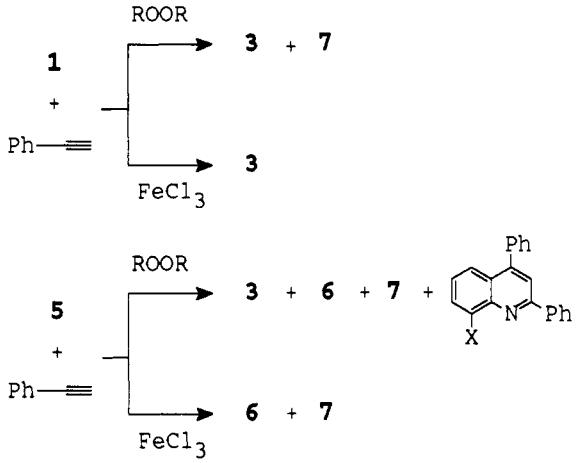


Table II. Reactions of Imines 5, Phenylacetylene, and Iron(III) Chloride in the Presence of Chloranil

imine	X	6 Yield,[a] %	7 Yield,[a] %	6/7
5a	MeO	43	36	1.2
5b	Cl	45	32	1.4
5c	Br	52	29	1.8
5d	O_2N	52	28	1.9

[a] All yields are for isolated pure products and are based on the starting imine.

Results and Discussion

Imines 1 (5 mmol) were allowed to react with phenylacetylene (50 mmol) in a boiling solution of anhydrous iron(III) chloride (11 mmol) in dry acetonitrile (30 mL).[10] After 30 min of reflux, ammonia was bubbled into the solution, and then the solvent was evaporated under vacuum and the residue was chromatographed on a silica gel column to give quinolines 3 and secondary amines 4 (Scheme I). The formation of imine reduction products

(1) Leardini, R.; Tundo, A.; Zanardi, G. *Synthesis* **1985**, 107.
(2) (a) Leardini, R.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1320. (b) Leardini, R.; Nanni, D.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1591. (c) Leardini, R.; Nanni, D.; Tundo, A.; Zanardi, G. *Gazz. Chim. Ital.* **1989**, *119*, 637.
(3) Leardini, R.; Nanni, D.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Chem. Commun.* **1989**, 757.
(4) Bachi, M. D.; Denenmark, D. *J. Am. Chem. Soc.* **1989**, *111*, 1886.
(5) Baine, N. H.; Qiang, L. G. *J. Org. Chem.* **1988**, *53*, 4218.
(6) For a comprehensive view of this topic, see: Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.
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(10) Iron(II) began to separate even before warmup of the mixture. Very good results were obtained with commercial anhydrous acetonitrile (Aldrich Chemie, $H_2O < 0.005\%$) without further purification. Use of iron(III) chloride hexahydrate and wet solvent lowered yields of products, probably because of partial hydrolysis of the starting imine; other high valence metal ion salts gave unsatisfactory results: for instance, cerium(IV) ammonium nitrate in acetonitrile or acetic acid solution produced lower yields of annulated products, and 1a in the presence of manganese(III) acetate gave a complex mixture in which only azobenzene could be identified.

Scheme V. Reaction of Imines 1 with Styrene and Iron(III) Chloride

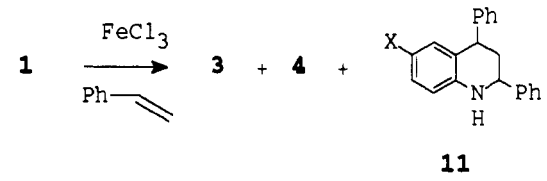

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Table III. Reactions of Imines 1 (Ar = C_6H_5), Styrene, and Iron(III) Chloride[a]

imine	X	3 Yield,[b] %	4 Yield,[b] %	11 Yield,[b] %
1a*	H	15	22	39
1b*	MeO	23	9	36
1c*	O_2N			99
1g*	EtOCO	25		60
1h*	MeCO	15		70
1i*	MeCONH	24	19	42
1j*	HO	51	5	9
1k*	NC			80
1a**	H	62		
1b**	MeO	68		
1i**	MeCONH	88		

[a] Reactions indicated by an asterisk were carried out in the absence of chloranil, whereas those indicated by a double asterisk were performed with addition of chloranil; in all annulations involving imine 1a, the final reaction mixture contained *N,N'*-diphenylbenzenecarboximidamide as well in about 10% yield. [b] All yields are for isolated pure products and are based on the starting imine.

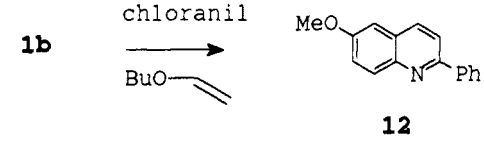
4 in an oxidizing medium was surprising, but could be rationalized by assuming initial formation of dihydro derivatives 2, which can be oxidized by starting imines to give aromatic compounds 3 and amines 4.[11] Such behavior is reported[12] for the reduction of Schiff bases by dihydroaromatic N-heterocycles. Dihydro intermediates 2 are also thought to be involved in the previously mentioned electrocyclic process that affords quinolines and reduction products of the starting *o*-alkenylimines.[5]

When stoichiometric amounts of chloranil[13] were added to the reaction mixture, imines 1 did not participate in the oxidation process leading from 2 to 3, and only quinolines 3 were obtained, in significantly higher yields (Table I).

The same reaction with imines 5, which bear a meta substituent on the aromatic ring linked to nitrogen, yielded a mixture of quinolines 6 and 7 in a substituent-dependent ratio, with a slight preference for 6 (Scheme II and Table II). With 8, in which the meta substituent is a pyridinic nitrogen atom, there was significant regioselectivity for naphthyridine 9 in preference to its isomer 10 (Scheme III).

This method does not work with other alkynes employed in corresponding radical reactions.[2,14] On the other hand, it appears applicable to a wide variety of functionalized imines, whereas the peroxide-mediated synthesis does not give good yields with nitro-substituted Schiff bases. Furthermore, the intermediate spiro radical formed in the cyclization of the adduct of imidoyl radicals and phenylacetylene[2b] leads to two isomeric quinolines from *N*-benzylidene-4-substituted anilines, whereas the same imines with iron(III) chloride give quinolines 3 exclusively. Analogously, imines 5 give only two isomers instead of four (Scheme IV).

Scheme VI. Reaction of Imine 1b with *n*-Butoxyethene and Chloranil



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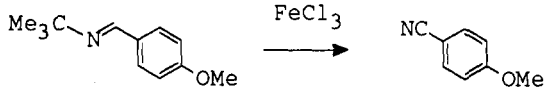
Scheme VII. Reaction of Imine 13 with Iron(III) Chloride



13 14 (10%)

Reaction of imines 1 (Ar = Ph) with styrene in a refluxing acetonitrile solution of iron(III) chloride gave mixtures of quinolines 3 (Ar = Ph), secondary amines 4 (Ar = Ph), and tetrahydroquinolines 11 (Scheme V and Table III).[15] Tetrahydroquinolines 11 were the principal products in every case except Schiff base 1j. They were the sole (1c, 1k) or strongly predominant (1g, 1h) products when X was an electron-withdrawing group. Addition of 2 equiv of chloranil to the reaction completely prevented formation of 4 and 11.

Reaction of imine 1a with vinyl acetate in the presence of iron(III) chloride and chloranil afforded 2-phenylquinoline (30%) with loss of the acetate group; thus, vinyl acetate might be useful in synthesizing quinolines with no substituent in the 4-position.[16]

We explored the possibility of performing the annulation without iron(III) chloride, using chloranil as the oxidizing agent. This reaction probably involves intermediate charge-transfer complexes between imines and chloranil, which have been studied by ESR spectroscopy with a variety of Schiff bases.[17] Imine 1b reacted with phenylacetylene and 1 equiv of chloranil to give quinoline 3b in 34% yield after 16 h of reflux. The same reaction with *n*-butoxyethylene afforded 6-methoxy-2-phenylquinoline (34%) after only 45 min of reflux (Scheme VI).

The involvement of an imine radical cation in this reaction is supported by the detection of significant amounts of Fe(II) ion in the final reaction mixture by ion-pair liquid chromatography,[18] as well as by the experiment shown in Scheme VII. Since ESR studies[7] have shown that radical cations similar to 13 fragment to *tert*-butyl radicals and nitriles, the formation of 14 is evidence for a one-electron oxidation process between an imine and Fe(III) ion.

The results shown in Scheme VIII argue against an acid-catalyzed mechanism in which iron(III) chloride acts as a Lewis acid. With imine 5d, the ratio of products

(11) Secondary amines 4 were not detected in a refluxing mixture of imine and iron(III) chloride in the absence of alkyne.

(12) van Niel, J. C. G.; Pandit, U. K. *J. Chem. Soc., Chem. Commun.* **1983**, 149 and references cited therein.

(13) For use of chloranil to aromatize nitrogen heterocycles, see: Braude, E. A.; Hannah, J.; Linstead, R. *J. Chem. Soc.* **1960**, 3249.

(14) A mixture of imine 1a and ethyl propiolate, refluxed for 48 h in the presence of iron(III) chloride, afforded starting material and trace amounts of *N,N'*-diphenylbenzenecarboximidamide, benzanilide, and other unidentified products. Better results were obtained with imine 1b and 3-methoxypropyne which, after 4 days reflux, gave 22% of 6-methoxy-4-(methoxymethyl)-2-phenylquinoline (see Experimental Section).

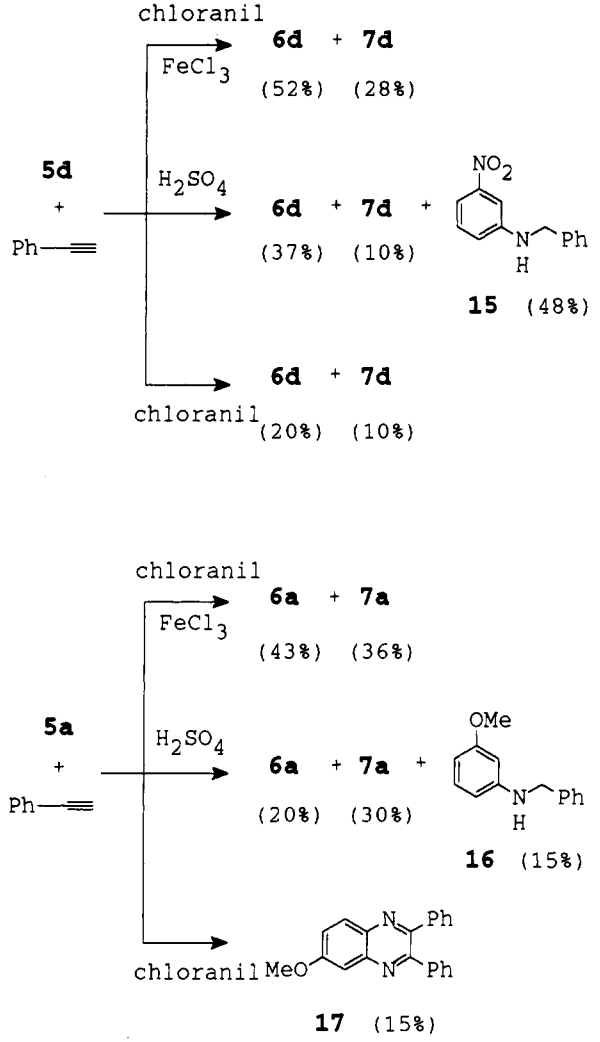
(15) Compounds 11 are not accessible by radical annulation of imines with styrene, and imines 1i and 1j cannot be used efficiently with peroxides because of hydrogen abstraction from phenolic or acetamidic groups.

(16) Other alkenes gave no results: acrylonitrile, methyl acrylate, and trimethoxysilylethene gave no reaction at all, and *n*-butoxyethylene reacted rapidly without heating to give only tars.

(17) Batyaev, I. M.; Gertman, G. A. *Deposited Doc.* **1977**, VINITI 4488 (*Chem. Abstr.* **1979**, *91*, 139920x). See also: Al-Ghabsha, T. S.; Azzouz, A. S.; Hassan, Y. I. *Microchem. J.* **1986**, *33*, 389 for studies of charge-transfer complexes of aromatic aldoximes with chloranil.

(18) This technique was chosen as a reliable method for determination of iron(II) concentration in the presence of iron(III) ions. Analyses carried out on reaction mixtures containing imine 1b and ferric chloride or imine 1b, ferric chloride, and phenylacetylene gave, respectively, [Fe(II)]/[Fe(III)] ratios of 0.43 and 0.67.

Scheme VIII. Comparison between the Reactions of Imines 5d and 5a in Acidic or Oxidant Medium



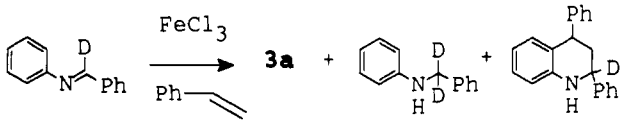
6d/7d obtained with iron(III) chloride (1.86) is significantly different from that obtained in an acid medium (3.70), but comparable to the ratio obtained in the chloranil-mediated reaction (1.94), in which it is presumed that only an oxidative mechanism can occur. With imine **5a**, the **6a**/**7a** ratio obtained with iron(III) chloride (1.19) differs from that obtained with acetic acid (0.67); comparison with the chloranil reaction is not possible because this reaction gave only quinoxaline **17**.

The possibility of an intermediate imidoyl radical, which could arise by proton loss from the imine radical cation, is unlikely because the reaction was not affected by a radical scavenger.[19] Moreover, imines substituted in the para position of the phenyl ring linked to nitrogen yielded only a single quinoline in both the iron and chloranil mediated reactions, whereas two isomers would be expected from a radical pathway. The reaction of imine **18**, styrene, and iron(III) chloride gave the tetrahydro derivative **20** with no detectable trace of the corresponding nondeuterated compound (Scheme IX), showing that the iminic C–H bond is not broken.

We surmise that our reaction might be regarded as an inverse-electron-demand Diels–Alder cycloaddition between the imine radical cation (diene) and the unsaturated C–C bond (dienophile). This hypothesis is supported by

(19) Imine **1b** and phenylacetylene afforded **3b** and **4b** in 55% and 14% yields, respectively, whereas, in the presence of 2,6-di-*tert*-butylphenol, the same products were formed in 47% and 16% yield.

Scheme IX. Reaction of Imine 18 with Styrene and Iron(III) Chloride



18 **19** **20**

reported examples of similar annulations involving radical cations and neutral molecules that are assumed to be Diels–Alder pericyclic reactions.[20]

Experimental Section

General Procedures. Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. ^{1}H-NMR spectra were recorded in deuteriochloroform on Varian EM 360L (60-MHz) or Varian Gemini 200 (200-MHz) instruments, using tetramethylsilane as an internal standard. Mass spectra and high-resolution mass spectra (HRMS) were performed with a VG 7070E spectrometer by electron impact with a beam energy of 70 eV. Column chromatography was performed on silica gel (ICN Silica 63–200 60A), using light petroleum (40–70 °C) and a light petroleum/diethyl ether gradient (from 0 up to 100% diethyl ether) as eluant. Previously reported reaction products were identified by spectral comparison and mixed mp determination with authentic specimens.

IPLC Chromatographic Determinations. IPLC chromatography was performed with a Waters 501 liquid chromatograph, using a C 18 column (Phenomenex 300 × 3.9 mm–10 μm) and a buffer solution (pH 3.40) of tartaric acid (40 mM) and octanesulfonic acid (2 mM) as eluant, with a flow rate of 2 mL/min. The eluted species were treated with the chromophoric complexing agent 4-(2-pyridilazo)resorcinol, monosodium salt (PAR) whose absorption was revealed by a Waters 484 UV/visible spectrophotometer at a wavelength of 520 nm.[21]

The reaction mixtures were allowed to reflux under nitrogen for 30 min, poured into aqueous acid, and extracted with diethyl ether; 500 μL of the aqueous phase was diluted to 50 mL, and 100 μL of the final solution was injected into the chromatographic system. The quantitative evaluation of iron(II) and iron(III) concentrations was achieved by using ferric and ferrous ion calibration plots; the resulting values were in the linearity range of the calibration.

Starting Materials. All reactions were performed in anhydrous acetonitrile (Aldrich Chemie, H_2O < 0.005%) using commercially available phenylacetylene (Aldrich Chemie), styrene (Aldrich Chemie), anhydrous iron(III) chloride (Farmitalia-Carlo Erba) and chloranil (Janssen Chimica).

Products **1a**,[22] **1b**,[23] **1c**,[24] **1d**,[25] **1e**,[26] **1f**,[27] **5a**,[28] **5b**,[29] **5c**,[30] **5d**,[31] **1g**,[32] **1h**,[33] **1i**,[34] **1j**,[35] **1k**,[36] **13**,[37] and **16**[38] were prepared according

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to the literature.

N-(Phenylmethylene)-5-amino-2-methoxypyridine (8). A benzene solution of 5-amino-2-methoxypyridine (3.72 g, 30 mmol) and benzaldehyde (3.18 g, 30 mmol) was refluxed for 2 h, with azeotropic removal of water, in the presence of *p*-toluenesulfonic acid (0.1 g). The solvent was evaporated and the residue distilled to give 8 in 85% yield; bp (10^{-3} mmHg) = 111–112 °C; mp = 47–49 °C (from 2-propanol); 60-MHz ^{1}H-NMR δ 3.87 (3 H, s, $-OCH_3$), 6.67 (1 H, d, J = 9 Hz, Ar-*H*), 7.20–7.97 (6 H, m, Ar-*H*), 8.07 (1 H, d, J = 2.5 Hz, Ar-*H*), 8.40 (1 H, s, -N=C*H*-); MS *m/e* 212 (M^+, 100), 211 (49), 197 (4), 183 (16), 182 (7); HRMS calcd for $C_{13}H_{12}N_2O$ 212.09496, found 212.09480. Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.57; H, 5.70; N, 13.20. Found: C, 73.53; H, 5.72; N, 13.22.

General Procedure for Reactions of Imines with Phenylacetylene or Styrene in the Presence of Iron(III) Chloride. To a solution of iron(III) chloride (1.78 g, 11 mmol) in acetonitrile (30 mL) were added the imine (5 mmol) and phenylacetylene (5.11 g, 50 mmol) or styrene (5.21 g, 50 mmol), and the resulting mixture was refluxed until a TLC analysis showed complete disappearance of the imine (30–45 min). The flask was cooled in an ice bath, and ammonia was bubbled into the mixture for about 2 min. The solvent was removed under vacuum in the presence of silica gel and the residue chromatographed to give the reaction products.

When chloranil was employed, it was added to the flask with the other reagents and the utilized amounts were 1.35 g (5.5 mmol) and 2.70 g (11 mmol) for phenylacetylene and styrene, respectively.

The following reactions were performed according to this general procedure.

Reaction of 1a with Phenylacetylene. **1a** (0.91 g) afforded 2,4-diphenylquinoline (**3a**) (0.65 g, 46%), mp = 112–113 °C (from light petroleum/benzene (80:20 v/v)) (lit.[2a] mp = 112–113 °C, mixed mp = 112–113 °C), and *N*-phenylbenzenemethanamine (**4a**) (0.20 g, 22%), mp = 37–38 °C (from light petroleum) (lit.[39] mp = 36 °C, mixed mp = 37–38 °C); *N,N'*-diphenylbenzenecarboximidamide (**21**) (0.15 g, 11%), mp = 143–145 °C (from ethanol) (lit.[40] mp = 144 °C, mixed mp = 143–145 °C).

Reaction of 1b with Phenylacetylene. **1b** (1.06 g) gave 6-methoxy-2,4-diphenylquinoline (**3b**) (0.86 g, 55%), mp = 121–122 °C (from light petroleum/benzene (80:20 v/v)) (lit.[2b] mp = 119–121 °C, mixed mp = 120–122 °C), and *N*-(4-methoxyphenyl)benzenemethanamine (**4b**) (0.15 g, 14%), mp = 50–52 °C (from light petroleum) (lit.[41] mp = 52 °C, mixed mp = 50–52 °C).

Reaction of 1c with Phenylacetylene. **1c** (1.13 g) gave 6-nitro-2,4-diphenylquinoline (**3c**) (0.99 g, 61%), mp = 208–210 °C (from ethanol/benzene (80:20 v/v)) [60-MHz ^{1}H NMR δ 7.40–7.70 (8 H, m, Ar-*H*), 8.00 (1 H, s, Ar-*H*), 8.17–8.53 (4 H, m, Ar-*H*), 8.90 (1 H, d, J = 2 Hz, Ar-*H*), MS *m/e* 326 (M^+, 100), 325 (13), 310 (3), 309 (3), 296 (14), 280 (44), 279 (86), 278 (19), 202 (24); HRMS calcd for $C_{21}H_{14}N_2O_2$ 326.105 53, found 326.103 96. Anal. Calcd for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58. Found: C, 77.35; H, 4.31; N, 8.56] and *N*-(4-nitrophenyl)benzenemethanamine (**4c**) (0.32 g, 28%), mp = 146–147 °C (from ethanol) (lit.[42] mp = 147 °C, mixed mp = 146–147 °C).

Reaction of 1a with Phenylacetylene and Chloranil. **1a** (0.91 g) afforded **3a** (1.07 g, 76%), mp = 112–113 °C (lit.[2a] mp = 112–113 °C, mixed mp = 112–113 °C), and **21** (0.1 g, 7%), mp = 144–145 °C (lit.[40] mp = 144 °C, mixed mp = 144–145 °C).

Reaction of 1b with Phenylacetylene and Chloranil. **1b** (1.06 g) yielded **3b** (1.09 g, 70%), mp = 120–122 °C (lit.[2b] mp = 119–121 °C, mixed mp = 120–122 °C).

Reaction of 1c with Phenylacetylene and Chloranil. **1c** (1.13 g) afforded **3c** (1.40 g, 86%), mp = 209–210 °C, spectral data are identical to those reported for compound **3c** obtained in the reaction of **1c** with phenylacetylene, and **4c** (0.02 g, 2%), mp = 146–147 °C (lit.[42] mp = 147 °C, mixed mp = 146–147 °C).

Reaction of 1d with Phenylacetylene and Chloranil. **1d** (1.13 g) gave 2-(4-nitrophenyl)-4-phenylquinoline (**3d**) (1.29 g, 79%), mp = 159–161 °C (from light petroleum/benzene (50:50 v/v)) (lit.[43] mp = 160 °C, mixed mp = 159–161 °C), and *N,N'*-diphenyl-4-nitrobenzenecarboximidamide (0.1 g, 6%), mp = 154–156 °C (from 2-propanol) (lit.[44] mp = 157 °C, mixed mp = 155–157 °C).

Reaction of 1e with Phenylacetylene and Chloranil. **1e** (0.94 g) afforded 4-phenyl-2-(2-thienyl)quinoline (**3e**) (0.86 g, 60%), mp = 83–85 °C (from light petroleum/benzene (90:10 v/v)) (lit.[45] mp = 85–86 °C, mixed mp = 84–86 °C).

Reaction of 1f with Phenylacetylene and Chloranil. **1f** (0.86 g) gave 2-(2-furyl)-4-phenylquinoline (**3f**) (0.75 g, 55%), mp = 100–102 °C (from light petroleum/benzene (90:10 v/v)) (lit.[45] mp = 103–103.5 °C, mixed mp = 100–103 °C).

Reaction of 5a with Phenylacetylene and Chloranil. **5a** (1.06 g) afforded 5-methoxy-2,4-diphenylquinoline (**6a**) (0.67 g, 43%), mp = 84–85 °C (from light petroleum/benzene (90:10 v/v)) (lit.[2b] mp = 84–85 °C, mixed mp = 84–85 °C), and 7-methoxy-2,4-diphenylquinoline (**7a**) (0.56 g, 36%), mp = 101–102 °C (from light petroleum/benzene (90:10 v/v)) (lit.[2b] mp = 100–101 °C, mixed mp = 101–102 °C).

Reaction of 5b with Phenylacetylene and Chloranil. **5b** (1.08 g) yielded 5-chloro-2,4-diphenylquinoline (**6b**) (0.71 g, 45%), mp = 111–112 °C (from light petroleum/benzene (90:10 v/v)) [200-MHz ^{1}H NMR δ 7.30–7.59 (10 H, m, Ar-*H*), 7.73 (1 H, s, Ar-*H*), 8.10–8.22 (3 H, m, Ar-*H*); MS *m/e* 317 (M^+ + 2, 33), 316 (M^+ + 1, 26), 315 (M^+, 97), 314 (17), 280 (100), 238 (6), 202 (18); HRMS calcd for $C_{21}H_{14}ClN$ 315.081 48, found 315.081 26. Anal. Calcd for $C_{21}H_{14}ClN$: C, 79.86; H, 4.47; Cl, 11.23; N, 4.44. Found: C, 79.82; H, 4.48; Cl, 11.25; N, 4.45] and 7-chloro-2,4-diphenylquinoline (**7b**) (0.50 g, 32%), mp = 95–96 °C (from light petroleum/benzene (90:10 v/v)) (lit.[2b] mp = 94–95 °C, mixed mp = 95–96 °C).

Reaction of 5c with Phenylacetylene and Chloranil. **5c** (1.30 g) gave 5-bromo-2,4-diphenylquinoline (**6c**) (0.94 g, 52%), mp = 93–94 °C (from light petroleum/benzene (90:10 v/v)) [200-MHz ^{1}H NMR δ 7.38–7.58 (9 H, m, Ar-*H*), 7.77 (1 H, dd, J = 8, 1.2 Hz, Ar-*H*), 7.82 (1 H, s, Ar-*H*), 8.16–8.30 (3 H, m, Ar-*H*); MS *m/e* 361 (M^+ + 2, 47), 360 (M^+ + 1, 17), 359 (M^+, 47), 280 (100), 278 (17), 202 (20), 176 (14), 140 (16); HRMS calcd for $C_{21}H_{14}BrN$ 359.030 96, found 359.030 74. Anal. Calcd for $C_{21}H_{14}BrN$: C, 70.01; H, 3.92; Br, 22.18; N, 3.89. Found: C, 70.04; H, 3.91; Br, 22.17, N, 3.88] and 7-bromo-2,4-diphenylquinoline (**7c**) (0.52 g, 29%), mp = 109–110 °C (from light petroleum/benzene (90:10 v/v)) [200-MHz ^{1}H NMR δ 7.44–7.58 (9 H, m, Ar-*H*), 7.75 (1 H, d, J = 9 Hz, Ar-*H*), 7.81 (1 H, s, Ar-*H*), 8.14–8.22 (2 H, m, Ar-*H*), 8.44 (1 H, d, J = 2.3 Hz, Ar-*H*); MS *m/e* 361 (M^+ + 2, 100), 360 (M^+ + 1, 92), 359 (M^+, 100), 358 (75), 280 (50), 279 (16), 278 (23), 203 (9), 202 (9), 201 (13), 176 (11), 140 (27); HRMS calcd for $C_{21}H_{14}BrN$ 359.030 96, found 359.030 78. Anal. Calcd for $C_{21}H_{14}BrN$: C, 70.01; H, 3.92; Br, 22.18; N, 3.89. Found: C, 70.06; H, 3.91; Br, 22.15; N, 3.88].

Reaction of 5d with Phenylacetylene and Chloranil. **5d** (1.13 g) afforded 5-nitro-2,4-diphenylquinoline (**6d**) (0.85 g, 52%), mp = 141–143 °C (from light petroleum/benzene (50:50 v/v)) [200-MHz ^{1}H NMR δ 7.35–7.60 (8 H, m, Ar-*H*), 7.70–7.80 (1 H, m, Ar-*H*), 7.87 (1 H, dd, J = 7.5, 1.4 Hz, Ar-*H*), 7.92 (1 H, s, Ar-*H*), 8.15–8.25 (2 H, m, Ar-*H*), 8.45 (1 H, dd, J = 8.2, 1.4 Hz, Ar-*H*); MS *m/e* 326 (M^+, 100), 309 (23), 296 (10), 281 (38), 280 (53), 202 (28), 176 (20), 78 (10); HRMS calcd for $C_{21}H_{14}N_2O_2$ 326.105 53, found 326.105 56. Anal. Calcd for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58. Found: C, 77.24; H, 4.33; N, 8.60] and 7-nitro-2,4-diphenylquinoline (**7d**) (0.46 g, 28%), mp = 180–182 °C (from light petroleum/benzene (50:50 v/v)) [200-MHz ^{1}H NMR δ 7.45–7.65 (8 H, m, Ar-*H*), 7.95 (1 H, s, Ar-*H*), 8.02 (1 H, d, J = 8.8 Hz, Ar-*H*), 8.13–8.25 (3 H, m, Ar-*H*), 9.07 (1 H, d, J = 2.3 Hz, Ar-*H*); MS *m/e* 326 (M^+, 100), 325 (49), 296 (5), 280 (25), 279 (28), 278 (13), 253 (7), 252 (11), 78 (21); HRMS calcd for $C_{21}H_{14}N_2O_2$ 326.105 53, found 326.105 24. Anal. Calcd for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58. Found: C, 77.23; H, 4.32; N, 8.60].

Reaction of 8 with Phenylacetylene and Chloranil. **8** (1.06 g) gave 6-methoxy-2,4-diphenyl-1,5-naphthyridine (**9**) (0.78 g, 50%), mp = 155–156 °C (from light petroleum/benzene (80:20

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v/v)) [200-MHz ^{1}H NMR δ 3.90 (3 H, s, $-OCH_3$), 7.08 (1 H, d, J = 9 Hz, Ar-*H*), 7.38–7.55 (6 H, m, Ar-*H*), 7.85–7.92 (2 H, m, Ar-*H*), 8.02 (1 H, s, Ar-*H*), 8.10–8.18 (2 H, m, Ar-*H*), 8.28 (1 H, d, J = 9 Hz, Ar-*H*); MS m/e 312 (M^+, 100), 311 (83), 297 (12), 296 (8), 283 (24), 282 (11), 281 (17), 268 (7); HRMS calcd for $C_{21}H_{16}N_2O$ 312.126 26, found 312.126 34. Anal. Calcd for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.69; H, 5.17; N, 8.99] and 6-methoxy-2,4-diphenyl-1,7-naphthyridine (**10**) (0.11 g, 7%), mp = 165–166 °C (from light petroleum/benzene (80:20 v/v)) [200-MHz ^{1}H NMR δ 3.98 (3 H, s, $-OCH_3$), 7.05 (1 H, s, Ar-*H*), 7.35–7.53 (8 H, m, Ar-*H*), 7.85 (1 H, s, Ar-*H*), 8.08–8.15 (2 H, m, Ar-*H*), 9.25 (1 H, s, Ar-*H*); MS m/e 312 (M^+, 100), 311 (65), 297 (2), 283 (34), 282 (17), 281 (13), 268 (4), 254 (9), 240 (18); HRMS calcd for $C_{21}H_{16}N_2O$ 312.126 26, found 312.126 34. Anal. Calcd for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.71; H, 5.17; N, 8.98].

Reaction of 1b with 3-Methoxypropyne and Chloranil. 1b (1.06 g) and 3-methoxypropyne (3.5 g) afforded, after 4 days of reflux, 6-methoxy-4-(methoxymethyl)-2-phenylquinoline (**23**) (0.31 g, 22%) mp = 99–101 °C (from light petroleum/benzene (80:20 v/v)): 60-MHz ^{1}H NMR δ 3.47 (3 H, s, $-CH_2OCH_3$), 3.87 (3 H, s, $ArOCH_3$), 4.83 (2 H, s, $-CH_2OCH_3$), 7.10–8.30 (9 H, m, Ar-*H*); MS m/e 279 (M^+, 100), 264 (10), 249 (22), 248 (29), 236 (11), 234 (24), 219 (8), 205 (24), 204 (27); HRMS calcd for $C_{18}H_{17}NO_2$ 279.125 93, found 279.125 65. Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.45; H, 6.12; N, 5.00.

Reaction of 1a with Styrene. 1a (0.91 g) gave **3a** (0.21 g, 15%), mp = 112–113 °C (lit.[2a] mp = 112–113 °C, mixed mp = 112–113 °C), **4a** (0.20 g, 22%), mp = 36–38 °C (lit.[39] mp = 36 °C, mixed mp = 36–38 °C), 1,2,3,4-tetrahydro-2,4-diphenylquinoline (**11a**) (0.56 , 39%), mp = 95–97 °C (from ethanol) (lit.[46] mp = 97–98 °C, mixed mp = 95–98 °C), and **21** (0.1 g, 7%), mp = 144–145 °C (lit.[40] mp = 144 °C, mixed mp = 144–145 °C).

Reaction of 1b with Styrene. 1b (1.06 g) afforded **3b** (0.36 g, 23%), mp = 121–122 °C (lit.[2b] mp = 119–121 °C, mixed mp = 120–122 °C), **4b** (0.09 g, 9%), mp = 51–52 °C (lit.[41] mp = 52 °C, mixed mp = 51–52 °C), and 1,2,3,4-tetrahydro-6-methoxy-2,4-diphenylquinoline (**11b**) (0.57 g, 36%), mp = 114–116 °C (from 2-propanol): 200-MHz ^{1}H NMR δ 2.10–2.37 (2 H, m, $-CH_2-$), 3.60 (3 H, s, $-OCH_3$), 3.87 (1 H, bs, $-NH-$), 4.25–4.37 (1 H, dd, J = 11.7, 6.4 Hz, ArC*H*Ph), 4.50–4.60 (1 H, dd, J = 10.4, 3.2 Hz, $-NHCHPh$), 6.28 (1 H, d, J = 2.8 Hz, Ar-*H*), 6.55 (1 H, d, J = 8.6 Hz, Ar-*H*), 6.65 (1 H, dd, J = 8.6, 2.8 Hz, Ar-*H*), 7.17–7.50 (10 H, m, Ar-*H*); MS m/e 315 (M^+, 100), 314 (16), 300 (15), 238 (10), 236 (7), 224 (12), 210 (6), 91 (6); HRMS calcd for $C_{22}H_{21}NO$ 315.162 31, found 315.161 83. Anal. Calcd for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.74; H, 6.73; N, 4.45.

Reaction of 1c with Styrene. 1c (1.13 g) gave 1,2,3,4-tetrahydro-6-nitro-2,4-diphenylquinoline (**11c**) (1.63 g, 99%), mp = 177–179 °C (from 2-propanol/benzene (80:20 v/v)): 200-MHz ^{1}H NMR δ 2.10–2.40 (2 H, m, $-CH_2-$), 4.15–4.28 (1 H, dd, J = 12.1, 5.1 Hz, ArC*H*Ph), 4.65–4.75 (1 H, dd, J = 11, 3.6 Hz, $-NHCHPh$), 5.00 (1 H, bs, $-NH-$), 6.48 (1 H, d, J = 8.9 Hz, Ar-*H*), 7.15–7.58 (11 H, m, Ar-*H*), 7.88 (1 H, dd, J = 8.9, 2.4 Hz, Ar-*H*); MS m/e 330 (M^+, 100), 329 (29), 314 (2), 283 (5), 253 (12), 252 (9), 251 (23), 239 (18); HRMS calcd for $C_{21}H_{18}N_2O_2$ 330.136 83, found 330.136 57. Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.38; H, 5.48; N, 8.46.

Reaction of 1g with Styrene. 1g (1.27 g) yielded 2,4-diphenyl-6-quinoline carboxylic acid ethyl ester (**3g**) (0.44 g, 25%), mp = 139–140 °C (from light petroleum/benzene (50:50 v/v)) [200-MHz ^{1}H NMR δ 1.37 (3 H, t, J = 7.2 Hz, $-OCH_2CH_3$), 4.40 (2 H, q, J = 7.2 Hz, $-OCH_2CH_3$), 7.40–7.63 (8 H, m, Ar-*H*), 7.87 (1 H, s, Ar-*H*), 8.10–8.35 (4 H, m, Ar-*H*), 8.68 (1 H, d, J = 1.1 Hz, Ar-*H*); MS m/e 353 (M^+, 100), 352 (6), 324 (44), 308 (33), 280 (44), 202 (17); HRMS calcd for $C_{24}H_{19}NO_2$ 353.141 58, found 353.142 06. Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.52; H, 5.43; N, 3.97] and 1,2,3,4-tetrahydro-2,4-diphenylquinoline-6-carboxylic acid ethyl ester (**11g**) (1.07 g, 60%), mp = 191–193 °C (from acetone) [200-MHz ^{1}H NMR δ 1.25 (3 H, t, J = 7.1 Hz, $-OCH_2CH_3$), 2.10–2.35 (2 H, m, $-CHCH_2CH-$), 4.10–4.30 (3 H, m, $-OCH_2CH_3$ + ArC*H*Ph), 4.50 (1 H, bs, $-NH-$), 4.60–4.70 (1 H, dd, J = 10.7, 3.4 Hz, $-NHCHPh$), 6.50 (1 H, d, J = 8.4 Hz, Ar-*H*), 7.15–7.50 (11 H, m, Ar-*H*), 7.70 (1 H, dd, J = 8.4, 2 Hz, Ar-*H*); MS m/e 357 (M^+, 100), 356 (20), 312 (13), 284 (5), 280 (11), 278 (16), 91 (13); HRMS calcd for $C_{24}H_{23}NO_2$ 357.172 88, found 357.173 09. Anal. Calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.59; H, 6.51; N, 3.93].

Reaction of 1h with Styrene. 1h (1.12 g) gave 1-(2,4-diphenyl-6-quinolinyl)ethanone (**3h**) (0.24 g, 15%), mp = 168–170 °C (from light petroleum/benzene (30:70 v/v)) [200-MHz ^{1}H NMR δ 2.60 (3 H, s, $-CH_3$), 7.47–7.62 (8 H, m, Ar-*H*), 7.90 (1 H, s, Ar-*H*), 8.18–8.30 (4 H, m, Ar-*H*), 8.53 (1 H, s, Ar-*H*); MS m/e 323 (M^+, 92), 308 (100), 280 (37), 202 (38), 176 (17); HRMS calcd for $C_{23}H_{17}NO$ 323.131 01, found 323.130 73. Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.50; H, 5.28; N, 4.23] and 1-(1,2,3,4-tetrahydro-2,4-diphenyl-6-quinolinyl)-ethanone (**11h**) (1.15 g, 70%), mp = 215–216 °C (from 2-propanol/benzene (50:50 v/v)) [200-MHz ^{1}H NMR δ 2.10–2.35 (5 H, m, $-CH_3$ + $-CH_2-$), 4.20–4.30 (1 H, dd, J = 11.9, 4.8 Hz, ArC*H*Ph), 4.60 (1 H, bs, $-NH-$), 4.63–4.72 (1 H, dd, J = 10.5, 2.8 Hz, $-NHCHPh$), 6.53 (1 H, d, J = 8.6 Hz, Ar-*H*), 7.20–7.45 (11 H, m, Ar-*H*), 7.62–7.70 (1 H, dd, J = 8.6, 1 Hz, Ar-*H*); MS m/e 327 (M^+, 100), 326 (22), 312 (25), 284 (4), 250 (10), 248 (19), 236 (9), 194 (15), 179 (8), 172 (8), 91 (11); HRMS calcd for $C_{23}H_{21}NO$ 327.162 31, found 327.162 03. Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.46; H, 6.44; N, 4.26].

Reaction of 1i with Styrene. 1i (1.19 g) afforded *N*-(2,4-diphenyl-6-quinolinyl)acetamide (**3i**) (0.41 g, 24%), mp = 192–194 °C (from acetone) [200-MHz ^{1}H NMR δ 2.00 (3 H, s, $-CH_3$), 7.30–7.55 (8 H, m, Ar-*H*), 7.75 (1 H, s, Ar-*H*), 7.82 (1 H, dd, J = 9.1, 2.3 Hz, Ar-*H*), 8.08–8.18 (4 H, m, Ar-*H*), 8.48 (1 H, bs, $-NH-$); MS m/e 338 (M^+, 100), 296 (98), 295 (51), 280 (10), 217 (7), 190 (11), 43 (18); HRMS calcd for $C_{23}H_{18}N_2O$ 338.141 91, found 338.141 63. Anal. Calcd for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.67; H, 5.35; N, 8.26], *N*-[4-[(phenylmethyl)-amino]phenyl]acetamide (**4i**) (0.23 g, 19%), mp = 166–167 °C (from acetone)[47] [200-MHz ^{1}H NMR δ 2.10 (3 H, s, $-CH_3$), 4.00 (1 H, bs, $-NHCH_2Ph$), 4.28 (2 H, s, $-NHCH_2Ph$), 6.52–6.60 (2 H, A part of AA'BB', J = 8.9 Hz, Ar-*H*), 7.08 (1 H, bs, $-CONH-$), 7.20–7.38 (7 H, m + B part of AA'BB', Ar-*H*); MS m/e 240 (M^+, 100), 198 (16), 197 (12), 107 (75), 91 (61); HRMS calcd for $C_{15}H_{16}N_2O$ 240.126 26, found 240.125 86. Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 75.03; H, 6.69; N, 11.64], and *N*-(1,2,3,4-tetrahydro-2,4-diphenyl-6-quinolinyl)acetamide (**11i**) (0.72 g, 42%), mp = 223–225 °C (from acetone) [200-MHz ^{1}H NMR δ 2.00 (3 H, s, $-CH_3$), 2.15–2.38 (2 H, m, $-CH_2-$), 4.03 (1 H, bs, $ArNHCHPh$), 4.20–4.32 (1 H, dd, J = 11.3, 6 Hz, ArC*H*Ph), 4.50–4.60 (1 H, dd, J = 10.6, 3.4 Hz, $-NHCHPh$), 6.42 (1 H, d, J = 1.1 Hz, Ar-*H*), 6.54 (1 H, d, J = 8.5 Hz, Ar-*H*), 6.82 (1 H, bs, $-CONH-$), 7.18–7.48 (11 H, m, Ar-*H*); MS m/e 342 (M^+, 100), 341 (15), 300 (9), 299 (17), 265 (11), 263 (9), 251 (8), 237 (8), 209 (13), 195 (12), 91 (16), 43 (16); HRMS calcd for $C_{23}H_{22}N_2O$ 342.173 21, found 342.173 29. Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48; N, 8.18. Found: C, 80.75; H, 6.46; N, 8.16].

Reaction of 1j with Styrene. 1j (0.99 g) gave 2,4-diphenyl-6-quinolinol (**3j**) (0.76 g, 51%), mp = 222–223 °C (from light petroleum/benzene (30:70 v/v)) (lit.[2b] mp = 222–223 °C, mixed mp = 222–223 °C), 4-[(phenylmethyl)amino]phenol (**4j**) (0.05 g, 5%), mp = 88–89 °C (from light petroleum/benzene (50:50 v/v)) (lit.[48] mp = 89–90 °C, mixed mp = 88–90 °C), and 1,2,3,4-tetrahydro-2,4-diphenyl-6-quinolinol (**11j**) (0.13 g, 9%), mp = 200–203 °C (from 2-propanol/benzene (50:50 v/v)): 200-MHz ^{1}H NMR δ 1.60 (1 H, bs, $-OH$), 2.08–2.33 (2 H, m, $-CH_2-$), 4.07 (1 H, bs, $-NH-$), 4.20–4.32 (1 H, dd, J = 11.5, 6.1 Hz, ArC*H*Ph), 4.48–4.57 (1 H, dd, J = 10.5, 3.3 Hz, $-NHCHPh$), 6.15 (1 H, d, J = 2.2 Hz, Ar-*H*), 6.48 (1 H, d, J = 8.4 Hz, Ar-*H*), 6.56 (1 H, dd, J = 8.4, 2.2 Hz, Ar-*H*), 7.15–7.48 (10 H, m, Ar-*H*); MS m/e 301 (M^+, 100), 300 (24), 286 (8), 224 (16), 222 (15), 210 (27),

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(47) Compound **4i** is described in two papers: ref 43 and Nose, A.; Kudo, T. *Chem. Pharm. Bull.* **1986**, *34*, 4817. The reported melting points (141–142 °C) differ significantly from what we found (166–167 °C); therefore, we decided to synthesize **4i** by reacting *N*-(4-aminophenyl)-acetamide and chlorophenylmethane. The physical and spectroscopic data comparison between **4i** and the two compounds obtained in this latter reaction confirmed the identification of **4i** as *N*-[4-[(phenylmethyl)amino]phenyl]acetamide, whereas the compound previously reported appears to be *N*-[4-[[bis(phenylmethyl)]amino]phenyl]acetamide.

(48) Bakunin, M. *Gazz. Chim. Ital.* **1906**, *36(II)*, 211.

196 (11), 91 (9); HRMS calcd for $C_{21}H_{19}NO$ 301.146 66, found 301.146 68. Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.80; H, 6.33; N, 4.64.

Reaction of 1k with Styrene. **1k** (1.03 g) yielded 1,2,3,4-tetrahydro-2,4-diphenyl-6-quinolinecarbonitrile (**11k**) (1.22 g, 80%), mp = 188–190 °C (from 2-propanol): 200-MHz ^{1}H NMR δ 2.10–2.40 (2 H, m, $-CH_2-$), 4.15–4.25 (1 H, dd J = 11.9, 4.7 Hz, ArC*H*Ph), 4.60–4.75 (2 H, m, -N*H*- + -NHC*H*Ph), 6.50 (1 H, d, J = 8.1 Hz, Ar-*H*), 6.85 (1 H, bs, Ar-*H*), 7.17–7.50 (11 H, m, Ar-*H*); MS m/e 310 (M^+, 100), 309 (31), 295 (7), 233 (17), 232 (13), 231 (41), 219 (55), 205 (17), 155 (21), 91 (20); HRMS calcd for $C_{22}H_{18}N_2$ 310.147 00, found 310.147 00. Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.02. Found: C, 85.09; H, 5.87; N, 9.04.

Reaction of 1a with Styrene and Chloranil. **1a** (0.91 g) afforded **3a** (0.87 g, 62%), mp = 112–113 °C (lit.[2a] mp = 112–113 °C, mixed mp = 112–113 °C), and **21** (0.12 g, 9%), mp = 144–145 °C (lit.[40] mp = 144 °C, mixed mp = 144–145 °C).

Reaction of 1b with Styrene and Chloranil. **1b** (1.06 g) gave **3b** (1.06 g, 68%), mp = 120–122 °C (lit.[2b] mp = 119–121 °C, mixed mp = 120–122 °C).

Reaction of 1i with Styrene and Chloranil. **1i** (1.19 g) gave **3i** (1.49 g, 88%), mp = 193–194 °C; spectral data are identical to those reported for compound **3i** obtained in the reaction of **1i** with styrene.

Reaction of 1a with Vinyl Acetate and Chloranil. **1a** (0.91 g) yielded 2-phenylquinoline (0.31 g, 30%), mp = 83–84 °C (from light petroleum) (lit.[49] mp = 85 °C, mixed mp = 83–85 °C).

Reaction of 1b with *n*-Butoxyethene and Chloranil in the Absence of Iron(III) Chloride. The general procedure described above was followed, but instead of bubbling in ammonia, the reaction mixture was treated with 10% aqueous sodium hydroxide and extracted with diethyl ether; the organic phase was dried (sodium sulfate), the solvent removed under vacuum, and the residue chromatographed to give 6-methoxy-2-phenylquinoline (**12**) (0.40 g, 34%), mp = 132–133 °C (from light petroleum/benzene (80:20 v/v)) (lit.[49] mp = 132 °C, mixed mp = 132–133 °C).

Reaction of 13 with Iron(III) Chloride. **13** gave, after 24 h of reflux, unreacted **13** (80%) and 4-methoxybenzonitrile (**14**) (0.08 g, 10%), mp = 60–61 °C (from light petroleum) (lit.[50] mp = 61–62 °C, mixed mp = 60–62 °C).

Reaction of 5d with Phenylacetylene in Acetic Acid. A solution of **5d** (1.13 g, 5 mmol) and phenylacetylene (5.11 g, 50 mmol) in acetic acid (30 mL) was kept at room temperature with magnetic stirring. After 1 h, sulfuric acid (0.30 mL) was added and the mixture maintained for 1 h at room temperature and then for 2 h at 70 °C. Acetic acid was partially removed under vacuum and the residue poured into water, neutralized with 10% aqueous sodium hydroxide, and extracted with diethyl ether; the organic phase was dried (sodium sulfate), the solvent removed, and the residue chromatographed to give **6d** (0.60 g, 37%), mp = 141–143 °C, **7d** (0.16 g, 10%), mp = 180–182 °C, and *N*-(3-nitrophenyl)benzenemethanamine (**15**) (0.55 g, 48%), mp = 106–107 °C (from ethanol) (lit.[51] mp = 107 °C, mixed mp = 106–107 °C).

Reaction of 5d with Phenylacetylene in the Presence of Chloranil. Following the procedure described for the reaction of **1b** with *n*-butoxyethene, **5d** (1.13 g), phenylacetylene (5.11 g), and chloranil (1.35 g) gave, after 7 days of reflux, **6d** (0.33 g, 20%), mp = 141–143 °C, and **7d** (0.17 g, 10%), mp = 180–182 °C.

Reaction of 5a with Phenylacetylene in Acetic Acid. Following the procedure described for the reaction of **5d** in acetic acid **5a** (1.06 g) afforded **6a** (0.31 g, 20%), mp = 84–85 °C (lit.[2b] mp = 84–85 °C, mixed mp = 84–85 °C), **7a** (0.47 g, 30%), mp = 101–102 °C (lit.[2b] mp = 100–101 °C, mixed mp = 100–102 °C), and *N*-(3-methoxyphenyl)benzenemethanamine (**16**) (0.16 g, 15%), bp (27 mmHg) = 225–227 °C (lit.[52] bp (27 mmHg) = 226–227 °C).

Reaction of 5a with Phenylacetylene in the Presence of Chloranil. Following the procedure described for the reaction of **1b** with *n*-butoxyethene, **5a** (1.06 g) gave, after 1 h of reflux, 6-methoxy-2,3-diphenylquinoxaline (**17**) (0.23 g, 15%), mp = 154–155 °C (from benzene) (lit.[53] mp = 154.5–155 °C, mixed mp = 154–155 °C).

Reaction of 1b with Phenylacetylene and Iron(III) Chloride in the Presence of 2,6-Di-*tert*-butylphenol. Following the general procedure described for the reactions carried out in acetonitrile, **1b** (1.06 g), phenylacetylene (5.11 g), iron(III) chloride (1.78 g), and 2,6-di-*tert*-butylphenol (2.27 g) afforded **3b** (0.73 g, 47%), mp = 121–122 °C (lit.[2b] mp = 119–121 °C, mixed mp = 120–122 °C), and **4b** (0.17 g, 16%), mp = 50–52 °C (lit.[42] mp = 52 °C, mixed mp = 50–52 °C).

Reaction of 18 with Styrene and Iron(III) Chloride. Following the general procedure described for the reactions carried out in acetonitrile, **18** (0.91 g), styrene (5.21 g), and iron(III) chloride (1.78 g) gave 2-deuterio-1,2,3,4-tetrahydro-2,4-diphenylquinoline (**20**) (0.60 g, 42%), mp = 95–97 °C (from ethanol, mixed mp with the analogous nondeuterated compound **11a** not depressed) [200-MHz ^{1}H NMR δ 2.15–2.30 (2 H, m, $-CH_2-$), 4.00 (1 H, bs, -N*H*-), 4.20–4.30 (1 H, dd, J = 11.4, 5.7 Hz, -C*H*Ph), 6.50–6.70 (3 H, m, Ar-*H*), 7.05–7.48 (11 H, m, Ar-*H*); MS m/e 286 (M^+, 100), 285 (21), 284 (10), 271 (8), 209 (19), 207 (13), 206 (22), 195 (35), 194 (26), 91 (11); HRMS calcd for $C_{21}H_{18}DN$ 286.158 03, found 286.157 85], and *N*-phenyl-α,α-dideuteriobenzenemethanamine (**19**) (0.10 g, 11%), which was not separated from **20** (the purity and the composition of the mixture was determined by GC analysis using the analogous nondeuterated compounds **11a** and **4a** as standards) [MS m/e 185 (M^+, 73), 184 (21), 108 (18), 93 (100), 77 (26), 51 (23); HRMS calcd for $C_{13}H_{11}D_2N$ 185.117 35, found 185.117 50], and **3a** (0.18 g, 13%), mp = 112–113 °C (lit.[2a] mp = 112–113 °C, mixed mp = 112–113 °C).

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Registry No. **1a**, 538-51-2; **1b**, 783-08-4; **1c**, 785-81-9; **1d**, 785-80-8; **1e**, 5918-68-3; **1f**, 3237-23-8; **1g**, 7182-99-2; **1h**, 24296-67-1; **1i**, 32746-39-7; **1j**, 588-53-4; **1k**, 17224-21-4; **3a**, 1039-51-6; **3b**, 5855-65-2; **3c**, 138432-74-3; **3d**, 1049-08-7; **3e**, 20364-68-5; **3f**, 20364-43-6; **3g**, 138432-75-4; **3h**, 138432-76-5; **3i**, 138432-77-6; **3j**, 5855-62-9; **4a**, 103-32-2; **4b**, 17377-95-6; **4c**, 14309-92-3; **4i**, 110137-65-0; **4j**, 103-14-0; **5a**, 5877-59-8; **5b**, 7519-65-5; **5c**, 20534-67-2; **5d**, 5341-44-6; **6a**, 87797-62-4; **6b**, 138432-78-7; **6c**, 138432-79-8; **6d**, 138432-80-1; **7a**, 87797-63-5; **7b**, 107931-51-1; **7c**, 138409-79-7; **7d**, 138409-80-0; **8**, 123534-01-0; **9**, 138409-81-1; **10**, 138409-82-2; **11a**, 30290-77-8; **11b**, 138409-83-3; **11c**, 138409-84-4; **11g**, 138409-85-5; **11h**, 138409-86-6; **11i**, 138409-87-7; **11j**, 138409-88-8; **11k**, 138409-89-9; **12**, 4789-73-5; **13**, 15875-74-8; **14**, 874-90-8; **15**, 33334-94-0; **16**, 90811-55-5; **17**, 26832-42-8; **18**, 3947-93-1; **19**, 136295-03-9; **20**, 138409-90-2; **21**, 2556-46-9; **23**, 138409-91-3; styrene, 100-42-5; vinyl acetate, 108-05-4; *n*-butoxyethene, 111-34-2; phenylacetylene, 536-74-3; 3-methoxypropyne, 627-41-8; iron(III) chloride, 7705-08-0; 5-amino-2-methoxypyridine, 6628-77-9; *N,N'*-diphenyl-4-nitrobenzenecarboximidamide, 19555-22-7; 2-phenylquinoline, 612-96-4.

Supplementary Material Available: ^{1}H-NMR spectra for compounds **6b**, **6c**, **7c**, **6d**, **7d**, **9**, **10**, **and 20** and structural arguments (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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