mixture with **5d**) resulted in rearrangement to **8** (see preparation of **5d**, below). Ether **8** was also obtained as the only identifiable product from the decomposition of **5b**.

A mixture of pure tosylate **5b** (560 mg, 1.58 mmol) and NaCN (147 mg, 3.00 mmol) in anhydrous dimethyl sulfoxide (5 mL) was heated in an oil bath for 2.5 h at 85–90 °C. The workup (see nitrile **24**) gave a colorless oil (239 mg) which appeared to be a mixture of **5d**, **10**, and **8** (ca. 5:3:2, respectively, by NMR). Bulb-to-bulb distillation at aspirator pressure (90–120 °C) gave a fraction (120 mg) containing mainly the ethers (**10**/**8**/**5d**, ca. 10:7:3). Further distillation at 1 torr (80–180 °C) gave a second fraction (119 mg, 35% recovered yield) containing mainly the desired nitrile **5d** (ethers ≤10%). A sample obtained by VPC (170 °C, t_r = 10 min) was used for identification: IR 2950 (s), 2820 (w), 2248 (w), 1472 (w), 1456 (w, split), 1422 (w, split), 1387 (w), 1356 (m), 1224 (w), 1200 (w), 1174 (w), 1092 (s), 1067 (m, split), 1038 (w), 939 (w), 928 (w), 849 (w) cm^{-1}; NMR δ 3.57 (s, with fine structure, 1 H), 3.33 (s, 3 H), 3.00–2.00 (m, 4 H), 2.00–1.20 (m, 6 H), 0.92 (s, 9 H); mass spectrum, m/z 209.1777 (M^+ calcd for $C_{13}H_{23}NO$, 209.1779). Varying reaction conditions did not improve the yield of **5d** appreciably (maximum 60% in crude mixture).

A mixture of **5b** and **5c** (ca. 56% **5c**) was treated with NaCN as above. Inspection of the crude mixture by NMR (ca. 50% **5c**, plus products from **5b**) revealed that **5c** was recovered unchanged. Attempted isolation of **5c** from the above mixture by VPC gave ether **8** as the major volatile product (ca. 55% of isolated material), characterized from the following data: IR 3075 (w), 2984, 2939, and 2888 (s, merged), 1473 (w), 1456 (m), 1386 (w), 1356 (w), 1240 (w), 1161 (w), 1127 (m), 1109 (m), 1089 (m), 947 (w) cm^{-1}; NMR δ 5.37 (br s, 1 H), 3.25 and 3.15 (s and m, 3 + 2 H), 2.40–1.20 (m, 8 H), 1.03 (s, 9 H); mass spectrum, m/z 182.1681 (M^+ calcd for $C_{12}H_{22}O$, 182.1670).

***endo*-4-*tert*-Butyl-6-oxabicyclo[3.2.1]octane (10).** Treatment of alcohol **18** with 1 equiv of *p*-toluenesulfonyl chloride in pyridine or with 1 equiv of $SOCl_2$ in CH_2Cl_2 (containing 1 equiv of pyridine) gave ether **10** as the major product. The colorless volatile liquid was isolated by VPC (120 °C, 7 min) and characterized as follows: IR 2950 (s), 2869 (s), 1475 (w), 1464 (w), 1448 (w), 1385 (w), 1363 (m, split), 1281 (w), 1255 (w), 1180 (w), 1163 (w), 1083 (m, split), 999 (w), 975 (w), 960 (w), 908 (w), 897 (w), 886 (w), 863 (m) cm^{-1}; NMR δ 4.28 (d, J = 6.0–6.5 Hz, 1 H), 3.65 (d, J = 2.0–2.5 Hz, 2 H), 2.27 (br s, 1 H), ~2.3–1.1 (m, 7 H), 0.87 (s, 9 H).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.38; H, 11.85.

Methyl 4-*tert*-Butyl-3-cyclohexenecarboxylate (11) and Methyl *cis*-4-*tert*-Butyl-*trans*-3-chlorocyclohexanecarboxylate (12). Oxalyl chloride (160 μL, 1.83 mmol) was added to a cold (ca. 5 °C) solution of acid **4a** (70 mg, 0.33 mmol) in benzene (0.5 mL). After 1 h at 0–5 °C, the IR spectrum of an aliquot revealed only an ester carbonyl and no acid chloride or starting material. Excess reagent and solvent were removed in vacuo. VPC (155 °C) of the residue gave two products, identified as **11** (54.4 mg, 84%; t_r 7 min)[4] and **12** (11.3 mg, 15%; t_r = 16 min). For **11**: IR 3080 (w), 2985 (s, split), 2890 (w), 2820 (w), 1738 (s), 1473 (w), 1455 (w), 1430 (m), 1355 (m), 1244 (w), 1220 (w), 1187 (w), 1156 (m), 1078 (w), 1062 (w), 1025 (m), 917 (w), 892 (w), 853 (m) cm^{-1}; NMR δ 5.43 (s, with fine structure, 1 H), 3.63 (s, 3 H), 2.65–1.37 (m, 7 H), 1.03 (s, 9 H). For **12**: IR 2978 (s), 2891 (w), 1737 (s), 1430 (w), 1389 (w), 1362 (w), 1240 (w), 1186 (m), 1162 (m), 1022 (w), 851 (m) cm^{-1}; NMR δ 4.33 (m, 1 H), 3.63 (s, 3 H), 3.10–2.50 (m, 1 H), 2.50–1.30 (m, 7 H), 1.00 (s, 9 H); mass spectrum (CI), m/z 233.1297 [$(M + H)^+$ calcd for $C_{12}H_{21}{}^{35}ClO_2$, 233.1347].

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Palladium(0)-Catalyzed Arylation of Olefins by Arylamines and an Alkyl Nitrite

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Various olefins were arylated by the combination of arylamines and *tert*-butyl nitrite under palladium catalysis in the presence of acid such as monochloroacetic or acetic. The reaction proceeded in good yields without serious effects from substituents on either the olefinic substrates or the arylamines, including 3-aminopyridine.

Recently we reported that palladium(0) effectively catalyzed the arylation of olefins by arenediazonium salts.[1] The arylation was applicable to olefins bearing either electron-releasing or -withdrawing group(s) but was limited to the diazonium salts which we were able to manipulate at room temperature. Preliminary study[2] suggested that the limitation could be overcome by the use of the combination of an arylamine and *tert*-butyl nitrite for the arylation. The present paper deals with the effects of reaction conditions and of substituents of both the olefins and the arylamines on the reaction.

Results and Discussion

Effects of Reaction Conditions and Substituents of Arylamines on Arylation of Styrene. Dropwise addition of *tert*-butyl nitrite in acetic acid to a stirred mixture of an arylamine, styrene, bis(dibenzylideneacetone)palla-

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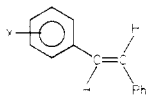
Table I. Effect of Reaction Conditions on Phenylation of Styrene by Aniline[a]

solvent (amt)	$Pd(dba)_2$, mol %	reaction temp, °C	yield,[b] %
CH_3CN-$ClCH_2COOH$ (20 mL/20 g)	10	*f*	43
CH_3COCH_3-$ClCH_2COOH$ (20 mL/20 g)	10	35	33
CH_2Cl_2-$ClCH_2COOH$ (20 mL/20 g)	10	*f*	66
CH_2Cl_2-$ClCH_2COOH$ (20 mL/20 g)	10	35	82
CH_2Cl_2-$ClCH_2COOH$ (20 mL/20 g)	5	35	53
CH_2Cl_2-$ClCH_2COOH$ (20 mL/20 g)	5	50	67
CH_3COOH (40 mL)	10	35	83
CH_3COOH-$ClCH_2COOH$ (20 mL/20 g)	5	50	97
CH_3COOH-$ClCH_2COOH$ (20 mL/20 g)	2	50	40
CH_3COOH-$Cl_2CHCOOH$ (20 mL/10 mL)	5	50	78[c]
CH_3COOH-CCl_3COOH (20 mL/20 g)	5	50	12[d]
CH_3COOH-CF_3COOH (20 mL/10 mL)	5	50	10[e]

[a] Reactions were performed with 10 mmol of aniline, 11 mmol of *tert*-butyl nitrite, and 20 mmol of styrene for 0.5 h. [b] Isolated yields based on aniline. Unless otherwise noted the product was (*E*)-stilbene. [c] About 5% of phenol and phenyl acetate were also formed. [d] Phenyl acetate (33%) was also formed. [e] Phenol (24%) and phenyl acetate (39%) were also formed. [f] Room temperature.

Table II. Arylation of Styrene by Arylamines[a] (Eq 1)



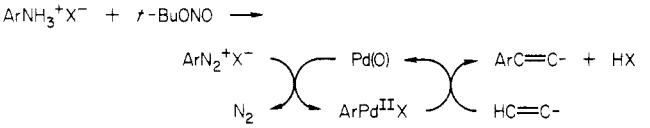
X	yield,[b] %	X	yield,[b] %
H	97	3-Cl	54
2-Me[c]	57	4-Cl	84
3-Me[c]	63	4-Br	61
4-Me	84	4-I	46
2-MeO[c]	87	2-NO_2	73
4-MeO	67	4-NO_2	79
2-Cl[c]	58	2-COOH[c,d]	46

[a] Unless otherwise noted the reactions were performed with 11 mmol of *tert*-butyl nitrite, 10 mmol of an arylamine, 0.5 mmol of $Pd(dba)_2$, and 20 mmol of styrene in acetic acid (20 mL)-monochloroacetic acid (20 g) at 50 °C for 0.5 h. [b] Isolated yields based on arylamine used. [c] 1.0 mmol of $Pd(dba)_2$ was used. [d] Acetic acid (40 mL) was used as the solvent.

dium(0) ($Pd(dba)_2$), and chloroacetic acid in acetic acid resulted in evolution of nitrogen (eq 1). The crude product

$$ArNH_2 + CH_2{=}CHPh + t\text{-}BuONO + Pd(dba)_2\ (5\text{ or }10\text{ mol }\%) \xrightarrow[50\ °C,\ 0.5h]{AcOH\text{-}ClCH_2COOH} ArCH{=}CHPh \quad (1)$$

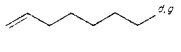
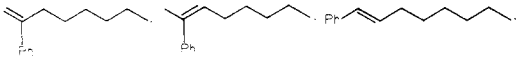
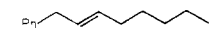
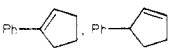
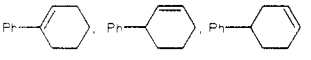
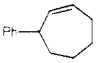
Scheme I[a]



[a] X^- = AcO^- or $ClCH_2COO^-$.

separated from the neutralized reaction mixture was purified by column chromatography followed by recrystallization or distillation. Effects of the reaction temperature and the medium on the phenylation with aniline are shown in Table I. The reaction in acetic acid–chloroacetic acid mixed solvent at 50 °C generally gave good results. The presence of chloroacetic acid was preferable for the success of the arylation, but a stronger acid such as trichloro- or trifluoroacetic acid decreased the yield of stilbene and produced phenol and/or phenyl acetate. The optimum reaction conditions, however, seem to be dependent on the nature of the arylamines and olefins (see Tables III and IV). Table II shows the results of the successful arylation of styrene with various arylamines. The good yields of the nitro-substituted products are noteworthy in view of the fact that arylation with *o*- or *p*-nitrobenzenediazonium tetrafluoroborate had afforded nitrobenzene as a main product (~30%) with only small amounts of arylated products (~10%).[1] Furthermore, the presence of an *o*-

Table III. Phenylation of Olefins by Aniline[a]

olefins	products[b]	yields, %[c]
	  (23:8:47:22)	61
	 (5:95)	81
	 (3:29:68)	43
		75
$CH_2{=}CHCOOEt$[d,f]	(*E*)-PhCH=CHCOOEt	79
$CH_2{=}CHCN$[d,g]	(*E*)-PhCH=CHCN, (*Z*)-PhCH=CHCN (70:30)	9
(*E*)-PhCH=CHCOOEt[d,g]	$(Ph)_2C{=}CCHCOOEt$	8

[a] Reactions were performed with 10 mmol of aniline, 11 mmol of *tert*-butyl nitrite, 20 mmol of an olefin, and 0.5 or 1.0 mmol of $Pd(dba)_2$ at 50 °C for 0.5 h. [b] Isomer distribution was determined by GLC. [c] Isolated yields based on aniline. [d] In acetic acid (40 mL). [e] In acetic acid (20 mL)-monochloroacetic acid (20 g). [f] With 0.5 mmol of $Pd(dba)_2$. [g] With 1.0 mmol of $Pd(dba)_2$.

nitro group is known to lower product yields in the Meerwein arylation.[3]

Arylation of Various Olefins by Aniline and 3-Aminopyridine. Aliphatic and alicyclic olefins, known to be poor substrates in the Meerwein arylation, were phenylated under similar conditions, as shown in Table III. The nature and the isomer distributions of the products were comparable with the results reported for other palladium-promoted arylations.[4-6] Even in the case of styrene and ethyl acrylate (good substrates in the Meerwein arylation) the present arylation gave better yields than those reported in the Meerwein arylation. Acrylonitrile, however, was a poor substrate in this palladium-catalyzed reaction. The successful results obtained with 3-aminopyridine, whose diazonium salt decomposes easily at room temperature, compare favorably with those obtained by the previous procedure via diazonium salts[1] (Table IV).

For ethyl acrylate and 1-octene, use of acetic acid only as solvent (at 50 °C) was preferable, since the combined medium, acetic acid and chloroacetic acid, caused the formation of unknown byproducts. A mixed-solvent system containing methylene chloride (which is known to be a good solvent for $Pd(dba)_2$) and chloroacetic acid at room temperature gave better results in the case of 3-aminopyridine.

Mechanism. The combination of an arylamine and an alkyl nitrite has been used in the Doyle modification of the Meerwein arylation[7] and in the Sandmeyer halogenation[8] with significant improvements. However, limitations remained on the olefinic substrates which could be used. Both the original and the modified Meerwein arylations are considered to proceed via an aryl radical intermediate as illustrated by eq 2 and 3, respectively. The nature of

$$ArN_2Cl \xrightarrow{Cu^{I}Cl} Ar\cdot \xrightarrow{CH_2=CHY} [ArCH_2\dot{C}HY] \xrightarrow{Cu^{II}Cl_2} ArCH=CHY \text{ and/or } ArCH_2CH(Cl)Y \quad (2)^3$$

$$ArNH_2 + t\text{-}BuONO + CH_2=CHY \rightarrow [ArCH_2\dot{C}HY] \xrightarrow{Cu^{II}X_2} ArCH_2CH(X)Y \quad (3)^7$$

X = Cl, Br; Y = Ph, CN, COOR, etc.

the copper-catalyzed reactions leads to the formation of addition and/or substitution products and to the requirement for the use of olefinic substrates activated with an electron-withdrawing group(s) in large excess.

Recently Oae et al. reported the arylation of olefins by the combination of arylamines and *tert*-butyl thionitrite or *tert*-butyl thionitrate in the presence of copper(II) halides (eq 4).[9] The reaction contains almost the same features as the Doyle system.

$$ArNH_2 + t\text{-}BuSNO + CH_2=CHY + CuX_2 \rightarrow ArCH_2CH(X)Y + ArX + t\text{-}Bu_2S_n \quad (4)$$

X = Cl, Br; Y = CN, COOR, Ph; n = 2,3

The nature of the present arylation is completely different from that of the copper-catalyzed (or promoted) reaction of arylamines; i.e., it gives no addition products and is free from the limitations on the olefinic substrates. Palladium(II) acetate promoted arylation[10] with an arylamine and *tert*-butyl nitrite has been reported but requires a stoichiometric amount of palladium and a long reaction time (8 h).

The reaction of an arylamine and an alkyl nitrite gives an aryl radical under neutral conditions,[7,11] whereas it affords a diazonium salt under acidic conditions. When styrene (20 mL) was arylated with aniline in acetonitrile (20 mL) instead of the acidic medium (chloroacetic acid–acetic acid), the reaction gave only 11% of stilbene along with tarry materials. In the present system, diazonium salts formed in situ may react with zerovalent palladium to give arylpalladium species, which are well-known to arylate olefins.[1,4] Several arylpalladium complexes have been isolated from the reaction of arenediazonium salts and tetrakis(triphenylphosphine)palladium(0) in the presence of anionic ligands such as halides.[12] Thus, Scheme I could account for the present arylation.

Aryl iodides have the highest reactivity in the reaction of aryl halides with zerovalent palladium to form arylpalladium species.[4] The formation of 4-iodostilbene from 4-iodoaniline suggests that the reactivity of the carbon–diazonium bond is higher than that of the carbon–iodine bond. Hence, the present reaction provides convenient method to form halo-substituted arylpalladium intermediates.

This procedure has several advantages as a synthetic method: (1) high product yields under mild conditions, (2) tolerance of substituents on both olefinic substrates (except for acrylonitrile) and arylamines.

Experimental Section

Materials. All solvents were distilled and stored under nitrogen. Guaranteed reagents of crystalline arylamines were used as received. Liquid arylamines were distilled under nitrogen before use. All olefins were used as received (styrene and ethyl acrylate contained *p-tert*-butylcatecol as an inhibitor for radical polymerization). Bis(dibenzylideneacetone)palladium(0) was prepared by published method.[13]

Arylation of Styrene. General Procedure. All procedures were carried out under nitrogen, although aerobic conditions also gave satisfactory results. To a mixture of 10 mmol of an arylamine, 20 mmol of styrene, 20 g of monochloroacetic acid, and 20 mL of acetic acid was added 0.5 mmol (or 1 mmol) of bis(dibenzylideneacetone)palladium(0). A solution of 11 mmol of *tert*-butyl nitrite in 10 mL of acetic acid was added dropwise to the mixture under stirring at 50 °C in a period of 15–20 min. Gas evolution started immediately and continued during the addition. After an additional 5–10 min of being stirred, the reaction mixture was neutralized by aqueous sodium carbonate and extracted with ether (3 × 100 mL). The combined extract was washed with aqueous sodium chloride and dried over magnesium sulfate. After removal of ether, *tert*-butyl alcohol, and excess styrene under reduced pressure, the residue was purified by column chromatography (silica gel–CCl_4 unless otherwise noted). This treatment gave pure stilbene and 4-methylstilbene. The other solid products except for 4-iodostilbene were recrystallized from ethanol after the column chromatography. 2-Methylstilbene was vacuum distilled. IR spectra of all products in Table II were pertinent to the expected structures and showed the characteristic ab-

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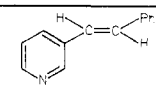
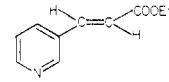
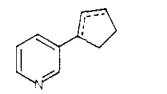
Table IV. Alkenylation of 3-Aminopyridine[a]

olefins	solvent (amt)	temp, °C	reaction products	yield,[b] %
CH_2=CHPh	AcOH-$ClCH_2COOH$ (20 mL/20 g)	50	 I	49
CH_2=CHPh	HCOOH (40 mL)	c	I	36
CH_2=CHPh	$CHCl_3$-$ClCH_2COOH$ (20 mL/20 g)	42	I	40
CH_2=CHPh	CH_2Cl_2-$ClCH_2COOH$ (20 mL/20 g)	42	I	64
CH_2=CHPh	CH_2Cl_2-$ClCH_2COOH$ (20 mL/20 g)	c	I	69
CH_2=CHCOOEt	CH_2Cl_2-$ClCH_2COOH$ (20 mL/20 g)	c		9
	CH_2Cl_2-$ClCH_2COOH$ (20 mL/20 g)	c		32

[a] Reactions were performed with 10 mmol of 3-aminopyridine, 11 mmol of *tert*-butyl nitrite, 20 mmol of an olefin, and 1 mmol of $Pd(dba)_2$ for 0.5 h. [b] Isolated yields based on 3-aminopyridine. [c] Room temperature.

sorption assigned to δ_{CH} of *trans*-CH=CH near 970 cm^{-1}. All the melting points in parentheses shown below were cited from the literature.[14]

(*E*)-Stilbene: mp 121.6–123.6 °C (lit. mp 124 °C); the IR spectrum was identical with that of the commercial compound. **(*E*)-2-Methylstilbene**, bp 117 °C (1.0 mmHg) [lit. mp 125 °C (1.5 mmHg)]. **(*E*)-3-Methylstilbene**, mp 48.6–49.4 °C (lit. mp 48 °C). **(*E*)-4-Methylstilbene**, mp 119.9–120.3 °C (lit. mp 119.5–120 °C). **(*E*)-2-Methoxystilbene**, mp 57.4–58.9 °C (lit. mp 59 °C). **(*E*)-4-Methoxystilbene**, mp 134.7–136.4 °C (lit. mp 136 °C). **(*E*)-2-Chlorostilbene**, mp 40.3–41.1 °C (lit. mp 39–40 °C). **(*E*)-3-Chlorostilbene**, mp 74.0–74.8 °C (lit. mp 73–74 °C). **(*E*)-4-Chlorostilbene**, mp 125.6–129 °C (lit. mp 129 °C). **(*E*)-4-Bromostilbene**, mp 136.0–138.7 °C (lit. mp 139 °C). **(*E*)-4-Iodostilbene**: pale green solid obtained from the column chromatography (alumina–benzene) was washed several times by hot diethyl ether to give pure white crystals; mp 148.4–151 °C (lit. mp 152 °C). **(*E*)-2-Nitrostilbene** (alumina–benzene), mp 71.8–72.4 °C (lit. mp 72 °C). **(*E*)-4-Nitrostilbene** (alumina–benzene), mp 149–153.8 °C (lit. mp 154.5–154.7 °C). **(*E*)-2-Carboxystilbene.** Acetic acid (40 mL) only was used as the solvent instead of the mixed medium, AcOH–$CH_2ClCOOH$. The reaction mixture was concentrated under reduced pressure, and the residue was recrystallized from ethanol; mp 158–159.6 °C (lit. mp 158–160 °C).

Phenylation of Olefins. The phenylation was carried out in acetic acid (40 mL) except for the cases of cyclopentene and cyclohexene, where the mixed solvent system, AcOH–$CH_2ClCOOH$, was employed. The structures of the products obtained from the cycloolefins and octene and their isomer distributions were determined by GLC analysis using the authentic samples prepared by another route (see ref 1 for cyclopentenes and cycloheptenes and ref 6 for phenyloctenes and phenylcyclohexenes). Hydrogenation of the phenylated cycloolefins gave the corresponding phenylcycloalkanes, which showed a single peak on GLC (silicone SE-30 or Ucon 50HB 5100). **Phenylcyclopentenes.** The ^1H NMR spectrum showed that a major isomer was 3-phenylcyclopentene.[1] **Phenylcyclohexenes.** ^1H NMR also supported the presence of 3- and 4-phenylcyclohexenes as major isomers assigned by GLC. **3-Phenylcycloheptene.** The GLC analysis showed a single peak along with a trace of phenylacetate: ^1H NMR (Me_4Si, CCl_4), 1.1–3.0 (m, 8 H), 3.5 (m, 1 H, benzylic), 5.57–5.90 (m, 2 H, olefinic), 7.04 (s, 5 H). **Ethyl cinnamate.** Both the IR spectrum and the retention time on GLC were identical with those of an authentic sample. **Cinnamonitrile.** IR, ^1H NMR, and GLC analysis showed the two isomers. The major one was identified as *trans*-cinnamonitrile by comparison of its retention time and ^1H NMR (5.65 ppm from Me_4Si, J = 16.2 Hz for an olefinic proton) with those of the authentic sample prepared by the Meerwein arylation of acrylonitrile. The minor one was reasonably assigned to *cis*-cinnamonitrile by the presence of an additional resonance in the ^1H NMR at 5.18 ppm with J = 12.0 Hz. **Ethyl 1,1-diphenylacrylate**: ^1H NMR (Me_4Si, $CDCl_3$), 1.05 (t, 3 H), 3.98 (q, 2 H), 6.29 (s, 1 H), 7.20 (s, 10 H).

Arylation by 3-Aminopyridine. Unless otherwise noted the reactions were performed in a mixed solvent system, CH_2Cl_2–$CH_2ClCOOH$, at room temperature. **3-Stilbazole (3-styrylpyridine)** (alumina–benzene): mp 81.4–83.0 °C; IR (Nujol) 970 cm^{-1} (*trans*-CH=CH); ^1H NMR (Me_4Si, $CDCl_3$) δ 7.04 (s, 2 H, HC=), 7.12–7.6 (m, 6 H, Ph ring protons and H^5 of pyridine ring), 7.74 (dt, 1 H, H^4), 8.44 (dd, 1 H, H^6), 8.69 (d, 1 H, H^2). Anal. Calcd for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73. Found: C, 85.59; H, 6.19; N, 7.65. **3-Pyridylcyclopentenes.** The ^1H NMR spectrum of the product showed the presence of 3-(3-pyridyl)cyclopentene as a major isomer (about 80%): δ 1.4–2.9 (m, 4 H), 3.6–4.0 (m, 1 H, benzylic), 5.55–6.0 (m, 2 H, olefinic), 6.9–7.5 (m, 2 H, H^4 and H^5 of pyridine ring), 8.30 (d, 2 H, H^2 and H^6). Hydrogenation of the product gave 3-pyridylcyclopentane; picrate, mp 126.2–128.7 °C (lit.[15] 128–128.7 °C). **Ethyl 3-(3-pyridyl)acrylate**: picrate, mp 154–157 °C; ^1H NMR (Me_4Si, $CDCl_3$), 1.31 (t, 3 H), 2.24 (q, 2 H), 6.44 (d, J = 16 Hz, 1 H), 7.23 (dd, 1 H, H^5), 7.62 (d, J = 16, 1 H), 7.74 (dt, 1 H, H^4), 8.52 (d, 1 H, H^6), 8.64 (s, 1 H, H^2).

Registry No. Styrene, 100-42-5; benzenamine, 62-53-3; 2-methylbenzenamine, 95-53-4; 3-methylbenzenamine, 108-44-1; 4-methylbenzenamine, 106-49-0; 4-methoxybenzenamine, 104-94-9; 2-methoxybenzenamine, 90-04-0; 2-chlorobenzenamine, 95-51-2; 3-chlorobenzenamine, 108-42-9; 4-chlorobenzenamine, 106-47-8; 4-bromobenzenamine, 106-40-1; 4-iodobenzenamine, 540-37-4; 2-nitrobenzenamine, 88-74-4; 4-nitrobenzenamine, 100-01-6; 2-aminobenzoic acid, 118-92-3; (*E*)-stilbene, 103-30-0; (*E*)-2-methylstilbene, 22257-16-5; (*E*)-3-methylstilbene, 14064-48-3; (*E*)-4-methylstilbene, 1860-17-9; (*E*)-2-methoxystilbene, 52805-92-2; (*E*)-4-methoxystilbene, 1694-19-5; (*E*)-2-chlorostilbene, 1657-52-9; (*E*)-3-chlorostilbene, 14064-43-8; (*E*)-4-chlorostilbene, 1657-50-7; (*E*)-4-bromostilbene, 13041-70-8; (*E*)-4-iodostilbene, 13041-71-9; (*E*)-2-nitrostilbene, 4264-29-3; (*E*)-4-nitrostilbene, 1694-20-8; (*E*)-2-carboxystilbene, 5079-90-3; bis(dibenzylideneacetone)palladium(O), 32005-36-0; *tert*-butyl nitrite, 540-80-7; 1-octene, 111-66-0; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; ethyl 2-propenoate, 140-88-5; 2-propenenitrile, 107-13-1; ethyl (*E*)-3-benzenepropenoate, 4192-77-2; 3-phenylcyclopentene, 37689-22-8; 3-phenylcyclohexene, 15232-96-9; 4-phenylcyclohexene, 4994-16-5; 3-phenylcycloheptene, 19217-54-0; 1-phenylcyclohexene, 771-98-2; (*E*)-3-benzenepropenenitrile, 1885-38-7; (*Z*)-3-benzenepropenenitrile, 24840-05-9; ethyl 1,1-diphenylacrylate, 17792-17-5; 2-phenyl-1-octene, 5698-49-7; (*E*)-2-phenyl-2-octene, 53109-16-3; (*E*)-1-phenyl-1-octene, 28665-60-3; (*E*)-1-phenyl-2-octene, 42079-83-4; 1-phenylcyclopentene, 825-54-7; 3-aminopyridine, 462-08-8; (*E*)-3-styrylpyridine, 5097-91-6; 3-(3-pyridyl)cyclopentene, 79121-17-8; 3-pyridylcyclopentane picrate, 79134-69-3; 1-(3-pyridyl)cyclopentene, 62113-25-1; ethyl (*E*)-3-(3-pyridyl)acrylate, 59607-99-7; ethyl (*E*)-3-(3-pyridyl)acrylate picrate, 59608-00-3.

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(15) Lochte, H. L.; Wheeler, E. N. *J. Am. Chem. Soc.* **1954**, *76*, 5548.