Registry No. 3, 32704-36-2; **4**, 78965-02-3; **5**, 78965-03-4; **6**, 79027-04-6; **7**, 78965-04-5; **8**, 78965-05-6; **9**, 79027-05-7; **10**, 78965-06-7; **11**, 79027-06-8; **12a**, 78965-07-8; **12b**, 78965-08-9; **13a** enedione, 78965-09-0; **13b** enedione, 78965-10-3; **14a**, 78965-11-4; **14b**, 78965-12-5; **15a**, 78965-13-6; **15b**, 78965-14-7; **16a**, 79027-07-9; **16b**, 79081-88-2; **17a**, 78965-15-8; **17b**, 78965-16-9; **17c**, 78965-17-0; **18a**, 79027-08-0; **18b**, 79027-09-1; **18c**, 79027-10-4; **19a**, 78965-18-1; **19b**, 78965-19-2; **19c**, 78965-20-5; **20a**, 79027-11-5; **20b**, 79027-12-6; **21a**, 78965-21-6; **21b**, 78965-22-7; **21c**, 78965-23-8; **22a**, 79027-13-7; **22b**, 79027-14-8; **22c**, 79027-15-9; **23a**, 78965-24-9; **23b**, 78965-25-0; **23c**, 78965-26-1; **24a**, 79027-16-0; **24b**, 79027-17-1; **24c**, 79027-18-2; **25a**, 78965-27-2; **26a**, 78965-28-3; **26b**, 79027-19-3; (*E*,*E*)-1,4-dichlorobutadiene, 3588-12-3; 9-isopropylidene-1,4-dihydro-1,4-methanonaphthalene, 7350-72-3.

Reaction of Diazonium Salts with Transition Metals. 6. Preparation of Mixed Acid Anhydrides from Arenediazonium Salts and Sodium Carboxylates under Palladium(0) Catalysis[1]

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The palladium(0)-catalyzed reaction of arenediazonium tetrafluoroborates with carbon monoxide and sodium carboxylates in acetonitrile at 25 °C gave mixed acid anhydrides, ArCOOCOR (Ar = 3-Me-Ph, 4-Me-Ph, 2-MeO-Ph, 4-Br-Ph, 4-I-Ph, 3-NO_2-Ph, 4-NO_2-Ph, and Ph; R = H, Me, Et, *t*-Bu, and Ph), in good yields. Homoaromatic acid anhydrides, $(ArCO)_2O$, were obtained by heating of ArCOOCOMe at 100–120 °C under vacuum. ArCOOCO-*t*-Bu can be utilized to obtain the corresponding arenecarboxamides by the reaction with some amines.

Recently we reported a convenient carboxylation of arenediazonium tetrafluoroborates, ArN_2BF_4 (1), with carbon monoxide and sodium acetate in the presence of $Pd(OAc)_2$.[2] The initial product in the carboxylation was proposed to be a mixed acid anhydride (3) in which one of the acyl groups came from 1 and another from the sodium carboxylate (2) (eq 1).[2,3]

$$\underset{1}{ArN_2BF_4} + CO + \underset{2}{RCOONa} + Pd(OAc)_2 \rightarrow \underset{3}{ArCOOCOR} \quad (1)$$

This paper presents a convenient preparation of the mixed acid anhydrides (3), especially those carrying various aliphatic acyl groups as one of the acyl components. Facile transformation of ArCOOCOMe to arenecarboxylic anhydrides, $(ArCO)_2O$ (4), and utilization of ArCOOCO-t-Bu to obtain arenecarboxamide, $ArCONR^1R^2$ (5) are also described.

Results and Discussion

Preparation of Mixed and Homo Acid Anhydrides. The reaction was carried out with 1 (10 mmol), 2 (15 mmol), $Pd(OAc)_2$ (0.1–0.2 mmol), and carbon monoxide (9 kg/cm^2) in acetonitrile (60 mL) at room temperature (25 °C) for 0.5 h. Since 1 reacts with 2 spontaneously in acetonitrile to form tarry materials in the absence of carbon monoxide, a precaution should be taken against contact of 1 with 2 until the reaction atmosphere has been replaced by carbon monoxide. After removal of precipitates, consisting of palladium black and sodium tetrafluoroborate, and concentration of the filtrate, the residue was extracted with hexane at 30–35 °C. The crystalline products precipitated on cooling and were collected, while the liquid products were obtained by removal of the solvent under vacuum. Although the liquid products could be distilled by rapid short-pass distillation except for benzoic formic anhydride, only benzoic acetic and *p*-toluic acetic anhydrides [40 °C (0.5 mmHg)] were obtained in almost pure form (~99%). HPLC analysis of the products showed the presence of only a trace of benzoic (or *p*-toluic) anhydride and acetanilide (or aceto-*p*-toluide). The anilide content was less than 0.1% as judged by elemental analysis in which nitrogen could not be detected. The formation of a trace amount of *N*-arylacetamides by the reaction of diazonium salts with acetonitrile will be described in a separate paper. Benzoic (or *p*-toluic) formic anhydride decomposed to benzoic acid during distillation (vide infra). Results are summarized in Table I. In most of the products, peak areas of each acyl (or aroyl) group in the ^{1}H NMR spectra were consistent with their 1:1 composition (last column of Table I). The presence of homo acid anhydrides was evaluated by a deviation of the area ratio from the expected value in the ^{1}H NMR spectra. The IR spectra of the products showed two carbonyl absorptions characteristic of acid anhydrides. Homo aliphatic acid anhydrides, which can be easily detected by carbonyl absorption near 1825 cm^{-1} in the IR spectra, could not be found in all products listed in Table I. The contamination with acids could be estimated by the presence of a carbonyl absorption near 1690 cm^{-1} in the IR and by the ^{1}H NMR resonance near 10–12 ppm (from Me_4Si in CCl_4; (see footnote in Table I). HPLC analysis of some liquid products also showed a few percent of benzoic anhydride and/or benzoic acid in the liquid products. The contamination of the crystalline products with acids or homo acid anhydrides was proved to be negligible by IR and NMR measurements. Some of the liquid products contained small amount of acids and/or homo acid anhydrides, but further purification of the mixed acid anhydrides was difficult because of their facile disproportionation by heat.[4] The disproportionation of both liquid and crystalline products proceeded easily on standing even at room temperature; i.e., considerably scrambled mixture of acid anhydrides were obtained within 1 day for liquid compounds

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(1) Part V: Yamashita, R.; Kikukawa, K.; Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1980**, *201*, 463.

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(4) Hurd, C. D.; Dull, M. F. *J. Am. Chem. Soc.* **1932**, *54*, 3430.

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Table I. Preparation of Mixed Acid Anhydrides 3

no.	XPhCOOCOR X	 R	yield,[a] %	mp (lit.), °C	major impurity[b] (%)	IR,[c] $\nu_{C=O}$, cm^{-1}	R:PhX ratio[d]
1	H	H	86[e]	liquid	PhCOOH (8)	1750, 1782	
2	H	Me	73[f]	liquid		1738, 1810	49:51
3	H	Et	71[e]	liquid	PhCOOH (8) $(PhCO)_2O$ (4)	1734, 1807	
4	H	*t*-Bu	84[e]	liquid	*t*-BuCOOH, PhCOOH, (13), $(PhCO)_2O$ (17)	1735, 1808	
5	3-Me	Me	84[e]	liquid	3-Me-C_6H_4COOH (13)	1733, 1812	
6	4-Me	H	74	30.5–31.5	4-Me-C_6H_4COOH (10)	1745, 1781	
7	4-Me	Me	42[f]	liquid		1736, 1809	50:50
8	2-MeO	Me	56[e]	liquid		1741, 1806	50:50
9	4-Br	Me	83	27		1735, 1810	51:49
10	4-Br	Ph	59	82.3–83.3 (82–93)[g]		1725, 1785	50:50
11	4-I	Me	68	66.3–67.3		1727, 1796	50:50
12	3-NO_2	Me	49	44.2–44.8		1730, 1813	50:50
13	4-NO_2	Me	65	78.3–75.2		1735, 1802	50:50
14	4-NO_2	Et	28	38.8–40		1736, 1812	50:50
15	4-NO_2	Ph	42	122.5–124 (130–130.5)[g]		1728, 1788	
16	1-naphthyl	Ph	45	85.3–86.8 (89.5–90.3)[g]		1708, 1772	51:49

[a] Isolated yields based on ArN_2BF_4. [b] Identified and calculated by peak area of ^1H NMR and HPLC analysis. ^1H NMR resonance for COOH (Me_4Si, CCl_4) δ 11.77 (for entry 1), 10.63 (entry 3), 10.6 (entry 4, 1.21 for methyl proton of *t*-BuCOOH), 11.3 (entry 5), 11.75 (entry 6). [c] Neat or Nujol mull. [d] Calculated from area ratio in ^1H NMR. [e] Yield of the crude concentrate (see text). [f] Yield after distillation; yields of the crude concentrates are 87% for entry 2 and 60% for entry 7. [g] Zeavin, J. M., Fisher, A. M. *J. Am. Chem. Soc.*, **1932**, *54*, 3738.

Table II. Preparation of Arenecarboxylic Anhydrides (4)

X of (X-PhCO)$_2$O	yield,[a] %	mp, °C	lit.[b] mp °C
H	72	44.6–45.2	42
3-Me	68	64.2–66	71–72
4-Me	64	95.5–96.5	95
2-MeO	42	50–51.5	62–63[c]
4-Br	67 (38)[d]	225.2–226.7	220, 215.3–216.1[c]
4-I	64	243.5–245	229
3-NO_2	39	158.8–160.5	162–163
4-NO_2	64	188.7–190	195–195.5, 188–189[c]

[a] Isolated yields based on ArN_2BF_4. [b] "Beilstein's Handbuch der Organischen Chemie". [c] Authentic samples prepared from the corresponding acid chloride and sodium salt. [d] Isolated yield obtained by direct heating of the reaction mixture.

Table III. Preparation of Aromatic Carboxamides from in Situ Prepared ArCOOCO-*t*-Bu

XPhCONR^{1}R^2 X	 R^1	 R^2	yield,[a] %	bp/mmHg (mp), °C	lit. bp/mmHg (mp), °C
H	Ph	H	78	(161.4–161.9)	(163)[b]
4-EtOCO	Ph	H	37	(163.5–165)	
H	Et	Et	53	110–111/6	150–151/15[c]
4-Me	Et	Et	56	103–104/3 (54–54.8)	163/17 (54)[d]
4-Br	Et	Et	43	128–131/3 (64–64.5)	(62.2–63.5)[e]
4-NO_2	Et	Et	45	155–159/2.5	213–214/18[d]
4-MeO	Et	Et	54	133–137/3	148/4[d]

[a] Isolated yields based on ArN_2BF_4. [b] "Merck Index", 9th ed. [c] "Beilstein's Handbuch der Organischen Chemie", III-9. [d] *Ibid.*, II-9. [e] Authentic sample prepared from 4-bromobenzoyl chloride and diethylamine.

or within 1 week for crystalline ones. Since IR spectra of the filtered reaction mixture (immediately after completion of the reaction; acetonitrile solution) showed only two absorptions at carbonyl region, the above-mentioned contaminants were assumed to form during isolation process.

Neither the substituent in the diazonium salt nor the type of sodium carboxylate affects the product yield materially. The formation of mixed acid anhydrides from all the combinations of 1 and 2 examined here may confirm the reaction scheme proposed in our previous paper.[2]

The facile disproportionation of ArCOOCOMe and volatility of acetic anhydride provide a convenient route to homo arenecarboxylic anhydrides (4).[3,4] Heating of 3 (R = Me) at 100–120 °C under reduced pressure gave 4 in good yields (eq 2) as shown in Table II. Although 4

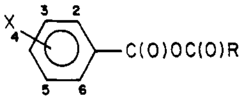
$$\underset{3}{ArCOOCOMe} \xrightarrow{100-120\ °C} \underset{4}{(ArCO)_2O} + Ac_2O \qquad (2)$$

was obtained by direct heating of the reaction mixture after removal of acetonitrile, the yields were lower than those from the isolated products 3. The conversion of 3 to 4 in an 80–98% yield also confirms the structure of 3. Since some products showed considerably different melting points from published values, authentic samples were prepared from corresponding sodium carboxylates and acid chlorides in acetonitrile. IR spectra of the authentic samples were completely superimposable with those of the products obtained through eq 2.

Arenecarboxylic formic anhydrides, ArCOOCHO, were easily decomposed to arenecarboxylic acid with evolution of carbon monoxide by heating at 100–120 °C.

In view of availability of various arylamines and the mild reaction conditions, the present procedure would provide a useful synthetic method for the mixed and the homo acid anhydrides. It could be compared very advantageously with the conventional transformation of diazonium salts to acid anhydrides via several steps, e.g., the Sandmeyer cyanation, hydrolysis, and dehydration (direct or through acid chlorides). The high reactivity of diazonium salts which allows the reaction to proceed under mild conditions would be a principal reason for the production of the thermally unstable mixed acid anhydrides. The formation

Table IV. ^{1}H NMR Spectral Data of Mixed Acid Anhydrides



			^{1}H NMR[a]		
no.	X	R	X	R	aromatic H
1	H	H		9.10 (s)	7.2–7.6 (m, 3–5), 7.95 (dd, 2, 6); $J_{2,3}$ = 8 Hz, $J_{2,4}$ = 1.7 Hz
2	H	Me		2.25 (s)	7.2–7.6 (m, 3–5), 7.91 (dd, 2, 6); $J_{2,3}$ = 8, $J_{2,4}$ = 1.7
3	H	Et		1.18 (t), 2.58 (q)	7.2–7.6 (m, 3–5), 7.90 (dd, 2, 6); $J_{2,3}$ = 8, $J_{2,4}$ = 1.7
4	H	*t*-Bu		1.31 (s)	7.2–7.6 (m, 3–5), 7.90 (dd, 2, 6); $J_{2,3}$ = 8, $J_{2,4}$ = 1.7
5	3-Me	Me	2.30 (s)	2.25 (s)	7.1–7.4 (m, 4, 5), 7.55–7.9 (m, 2, 6)
6	4-Me	H	2.37 (s)	9.05 (s)	7.14 (d, 3, 5), 7.82 (d, 2, 6); J = 8
7	4-Me	Me	2.37 (s)	2.25 (s)	7.14 (d, 3, 5), 7.79 (d, 2, 6); J = 8
8	2-MeO	Me	3.75 (s)	2.15 (s)	6.8–7.8 (m, 3, 5), 7.38 (dt, 4), 7.70 (dd, 6); $J_{3,4}$ = $J_{4,5}$ = 7.2, $J_{5,6}$ = 7.9, $J_{4,6}$ = 1.9
9	4-Br	Me		2.33 (s)	7.53 (d, 3, 5), 7.82 (d, 2, 6); J = 8.5
10[b]	4-Br	Ph		7.4–7.7 (m), 8.04 (dd), $J_{2',3'}$ = 7.7, $J_{2',4'}$ = 1.6	7.57 (d, 3, 5), 7.92 (d, 2, 6); J = 8.7
11	4-I	Me		2.32 (s)	7.66 (d, 3, 5), 7.76 (d, 2, 6); J = 8.7
12	3-NO_2	Me		2.35 (s)	7.60 (t, 5), 8.20 (dt, 6), 8.43 (dq, 4), 8.63 (dd, 2); $J_{4,5}$ = $J_{5,6}$ = 7.3, $J_{2,6}$ = $J_{4,6}$ = 1.3, $J_{2,4}$ = 2.0
13	4-NO_2	Me		2.41 (s)	8.24 (s)
14	4-NO_2	Et		1.28 (t), 2.69 (q)	8.22 (s)
15[c]	4-NO_2	Ph		7.4–7.7 (m), 7.95 (dd); $J_{2',3'}$ = 7.3, $J_{2',4'}$ = 2.7	8.15 (d, 3, 5), 8.28 (d, 2, 6); J = 7.9
16[b]	1-naphthyl	Ph		7.3–7.9 (m), 7.9–8.4 (m), 9.05 (dd, 8); $J_{7,8}$ = 6, $J_{7,8}$ = 2.5	

[a] In parts per million from Me_4Si in CCl_4 (60 MHz). Multiplicity and assignment as numbering on aromatic ring are shown in parentheses. Coupling constants are shown in hertz. [b] In $CDCl_3$. [c] In Me_2SO-d_6.

of iodo- or bromo-substituted products shows the higher reactivity of the diazonium group to zero-valent palladium than that of aryl halides.

Preparation of Arenecarboxamides. The aroyl component in mixed acid anhydrides is known to be less reactive toward a nucleophile than the acyl group. Thus, addition of aniline at room temperature to the filtered reaction mixture from benzenediazonium tetrafluoroborate and sodium acetate gave acetanilide as the main product in a molar ratio of 0.09 (PhCONHPh/MeCONHPh) (eq 3).[2] Replacement of sodium acetate with sodium mono-

$$\mathrm{ArCOOCOR} + \mathrm{R^1R^2NH} \rightarrow \mathrm{ArCONR^1R^2} + \mathrm{RCONR^1R^2} \qquad (3)$$

chloroacetate or isobutyrate improved the molar ratio slightly to 0.18 and 1.1, respectively. Use of sodium 2,2-dimethylpropanoate, a sterically hindered carboxylate, proved to be promising, and preferential formation of benzanilide (PhCONHPh/*t*-BuCONHPh ratio of 6–58, varies with the reaction conditions) was attained. The higher product ratio was realized by a slow addition of aniline to the cooled reaction mixture, since the exothermic nature of the reaction was apt to assist side reactions. When sodium benzoate instead of sodium 2,2-dimethylpropanoate was used in this reaction, an 86% yield of benzanilide was isolated. Typical results obtained with use of sodium 2,2-dimethylpropanoate are shown in Table III. All products, except for entry 26, showed the same IR spectra as those of the authentic samples prepared from corresponding acid chloride and amines. 4-(Ethoxycarbonyl)benzanilide showed satisfactory elemental analysis.

Experimental Section

IR or ^{1}H NMR spectra were measured by using a JASCO Model A-100 spectrometer or Hitachi R24B NMR spectrometer, respectively. A radial Pak A (C_{18}) cartridge (Waters Inc.) was used in HPLC analysis with an eluant of aqueous acetonitrile (30% H_2O).

Materials. Acetonitrile was distilled from phosphorus pentoxide (twice) and calcium hydride under nitrogen. Liquid arylamines were distilled before use under nitrogen. Guranteed reagents of crystalline arylamines were used as received. Arenediazonium tetrafluoroborates were prepared by the ordinary method[5] and stored under nitrogen at -20 °C. Palladium acetate was prepared by the published method.[6]

General Procedure for Preparation of Mixed Acid Anhydrides (3). A mixture of RCOONa (15 mmol), $Pd(OAc)_2$ (0.1–0.2 mmol), and acetonitrile (60 mL) was placed in a 300-mL glass autoclave and ArN_2BF_4 (10 mmol) wrapped in a poly(vinylidene chloride) film (Saran film) was held loosely above the liquid surface by using a stirring rod. Fine black powder formed by introduction of carbon monoxide (9 kg/cm^{-2}) disappeared immediately on mixing the diazonium salt with the solution. The mixture was then stirred at room temperature for 0.5 h. The introduction of diazonium salts was performed by rotating the stirring rod containing the salts loosely wrapped in a piece of Saran film. The completion of reaction can be easily discerned by the

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[5] Roe, A. *Org. React.* **1949**, *5*, 193.

[6] Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

appearance of a black dispersion (may be palladium black), and most of the reaction was completed within 20 min. After the carbon monoxide was purged, the reaction mixture was filtered, and the solvent was removed at 0 °C under vacuum. The residue was extracted several times with hexane at 30–35 °C when a sodium aliphatic carboxylate was used. The products were obtained by crystallization of the cooled hexane extracts or by removal of hexane under vacuum. When sodium benzoate was used, the solid residue was washed successively with small amounts of acetonitrile, water, and petroleum ether at 0 °C and dried under vacuum. Rapid short-pass distillation below 50 °C (bath temperature) in vacuo (0.5 mmHg) gave almost pure products in the case of benzoic acetic and *p*-toluic acetic anhydride with about 80% recovery. Since the purity of the distillates of other liquid products was similar to that of the crude concentrates, the yields of entries 1 and 3–5 listed in Table I were those of the concentrates. ^{1}H NMR spectral data of mixed acid anhydrides are summarized in Table IV. The characteristic features in IR and ^{1}H NMR spectra caused by the contamination with homo acid anhydrides and acids are described in the text and the footnote of Table I. Anal. PhCOOCOMe, calcd for $\mathrm{C_9H_8O_3}$: C, 68.85; H, 4.88. Found: C, 66.16; H, 4.88. 4-I-C$_6$H$_4$COOCOMe, calcd for $\mathrm{C_9H_7O_3I}$: C, 37.27;, H, 2.43. Found: C, 37.14; H, 2.43. 3-NO$_2$-C$_6$H$_4$COOCOMe, calcd for $\mathrm{C_9H_7NO_3}$: C, 51.68; H, 3.37; N, 6.70. Found: C, 51.66; H, 3.37; N, 7.00. 4-NO$_2$-C$_6$H$_4$COOCOMe, calcd: C, 51.68; H, 3.37; N, 6.70. Found: C, 51.33; H, 3.24; N, 6.96.

The structure of **3** (R = Ph) was also confirmed by comparison of IR spectra with those of authentic samples prepared by a published method.[7]

Arenecarboxylic Anhydrides (4). An arenecarboxylic acetic anhydride (1 g) was placed in a 30-mL round-bottomed flask and heated at 100–120 °C for 0.5–1 h under vacuum (ca. 10 mmHg), and the residue was distilled by means of a Kugelrohr distillation apparatus (ca. 3 mmHg). The structures of compounds **4** were confirmed by comparison of IR spectra with those of authentic samples prepared by the ordinary method from the corresponding arenecarboxylic acid.

Aromatic Carboxamides. To a filtered mixture (see the general procedure) was added an amine (3 mL) at 0 °C, and the mixture was stirred for 2 h at room temperature. After removal of the solvent, 100 mL of ether was added, and the mixture was washed with aqueous sodium carbonate, 1 N hydrochloric acid, and aqueous sodium chloride, and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was recrystallized (for anilides) or distilled (for *N*,*N*-diethyl amides).

Satisfactory IR and ^{1}H NMR spectra were obtained for all products produced by this method. For 4-EtOCO-C$_6$H$_4$CONHPh: ^{1}H NMR (Me$_4$Si, CDCl$_3$), 1.43 (t, 3 H), 4.38 (q, 2 H, J = 7 Hz), 7.1–7.7 (m, 5 H), 7.88 (d, 2 H), 8.08 ppm (d, 2 H, J = 9 Hz). Anal. Calcd for $\mathrm{C_{16}H_{15}NO_3}$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.03; H, 5.64; N, 5.15.

Registry No. **1** (Ar = Ph), 369-57-3; **1** (Ar = 3-MeC$_6$H$_4$), 1422-76-0; **1** (Ar = 4-MeC$_6$H$_4$), 459-44-9; **1** (Ar = 2-MeOC$_6$H$_4$), 492-95-5; **1** (Ar = 4-BrC$_6$H$_4$), 673-40-5; **1** (Ar = 4-IC$_6$H$_4$), 1514-50-7; **1** (Ar = 3-NO$_2$C$_6$H$_4$), 586-36-7; **1** (Ar = 4-NO$_2$C$_6$H$_4$), 456-27-9; **1** (Ar = 1-naphthyl), 28912-93-8; **2** (R = H), 141-53-7; **2** (R = Me), 127-09-3; **2** (R = Et), 137-40-6; **2** (R = Bu-*t*), 1184-88-9; **2** (R = Ph), 532-32-1; **3** (Ar = Ph; R = Me), 2819-08-1; **3** (Ar = 4-IC$_6$H$_4$; R = Me), 75474-02-1; **3** (Ar = 3-NO$_2$C$_6$H$_4$; R = Me), 4015-57-0; **3** (Ar = 4-NO$_2$C$_6$H$_4$; R = Me), 75474-03-2; **3** (Ar = Ph; R = H), 78823-32-2; **3** (Ar = Ph; R = Et), 50998-43-1; **3** (Ar = Ph; R = Bu-*t*), 19820-60-1; **3** (Ar = 3-MeC$_6$H$_4$; R = Me), 78823-33-3; **3** (Ar = 4-MeC$_6$H$_4$; R = H), 78823-34-4; **3** (Ar = 4-MeC$_6$H$_4$; R = Me), 75474-00-9; **3** (Ar = 2-MeOC$_6$H$_4$; R = Me), 78823-35-5; **3** (Ar = 4-BrC$_6$H$_4$; R = Me), 75474-01-0; **3** (Ar = 4-BrC$_6$H$_4$; R = Ph), 75474-04-3; **3** (Ar = 4-NO$_2$C$_6$H$_4$; R = Et), 78823-36-6; **3** (Ar = 4-NO$_2$C$_6$H$_4$; R = Ph), 75474-05-4; **3** (Ar = 1-naphthyl; R = Ph), 73368-15-7; **4** (Ar = Ph), 93-97-0; **4** (Ar = 3-MeC$_6$H$_4$), 21436-44-2; **4** (Ar = 4-MeC$_6$H$_4$), 13222-85-0; **4** (Ar = 2-MeOC$_6$H$_4$), 794-94-5; **4** (Ar = 4-BrC$_6$H$_4$), 1633-33-6; **4** (Ar = 4-IC$_6$H$_4$), 75474-06-5; **4** (Ar = 3-NO$_2$C$_6$H$_4$), 69859-37-6; **4** (Ar = 4-NO$_2$C$_6$H$_4$), 902-47-6; 4-EtOCOC$_6$H$_4$COOCO-*t*-Bu, 78823-37-7; 4-MeC$_6$H$_4$COOCO-*t*-Bu, 78823-38-8; 4-BrC$_6$H$_4$COOCO-*t*-Bu, 78823-39-9; 4-NO$_2$C$_6$H$_4$COOCO-*t*-Bu, 78823-40-2; 4-MeOC$_6$H$_4$COOCO-*t*-Bu, 78823-41-3; PhCONHPh, 93-98-1; 4-EtOCOC$_6$H$_4$CONHPh, 78823-42-4; PhCONEt$_2$, 1696-17-9; 4-BrC$_6$H$_4$CONEt$_2$, 5892-99-9; 4-MeC$_6$H$_4$CONEt$_2$, 2728-05-4; 4-NO$_2$C$_6$H$_4$CONEt$_2$, 5323-47-7; 4-MeOC$_6$H$_4$CONEt$_2$, 7465-86-3; Pd, 7440-05-3; PhNH$_2$, 62-53-3; Et$_2$NH, 109-89-7.

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Ortho Vinylation of Aromatic Amides via Cyclopalladation Complexes[1]

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The reaction of acetanilide and meta- and para-substituted acetanilides with palladium acetate has given new ortho-palladated complexes **2a–j**, which reacted with carbon monoxide, ethylene, or methyl vinyl ketone to produce the corresponding *N*-acylanthranilic esters **4a–m**, 2-acetaminostyrenes **9k–p**, and 4-aryl-3-buten-2-one derivatives **9a–j**, respectively. Reactions of **2a** with substituted olefins proceeded readily to give the 2-[(acetylamino)phenyl] olefins **8a–h**. Ortho-substituted acetanilides and *N*-methylacetanilide did not undergo complex formation with palladium acetate.

Investigations of ortho-metalated complexes of various aromatic compounds[2] have opened new routes in organic synthesis. Reactions of carbon monoxide[3] or isocyanide[4] with metal complexes of α-aryl nitrogen derivatives have led to syntheses of heterocyclic compounds. Reaction of ortho-palladated complexes with organolithium or Grignard reagents results in regiospecific carbon–carbon bond formation.[5] Insertion reactions with olefins[6] or acetylenes[7]

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