Arylation of Aromatic Heterocycles with Arenes and Palladium(II) Acetate

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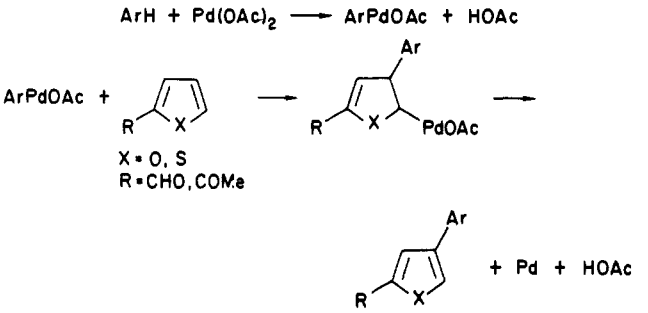
Treatment of aromatic heterocycles such as furfural, 2-acetylfuran, 2-formylthiophene, 2-acetylthiophene, 1-benzoylpyrrole, 1-(2,6-dichlorobenzoyl)pyrrole, 1-acetylindole, and 1-acetyl-3-methylindole with arenes and palladium(II) acetate gave the corresponding aryl-substituted aromatic heterocycles.

Aryl-substituted aromatic heterocycles are interesting compounds as precursors to biologically and physiologically active compounds and also in connection with the existence of naturally occurring compounds such as pterofuran,[1] 2-phenyl-5-propynylthiophene,[2] and 3,4,5-tribromo-2-(3,5-dibromo-2-hydroxyphenyl)pyrrole.[3] Oxidative coupling between aromatic heterocycles and arenes is an efficient and simple method for the preparation of the aryl-substituted aromatic heterocycles. On the other hand, oxidative dimerization of arenes[4] and of aromatic heterocycles such as furans,[5,6] thiophenes,[6,7] and 1-benzoylpyrroles[8] are known to be accomplished by palladium(II) salts. However, no report of oxidative cross-coupling between aromatic heterocycles except isoxazoles[9] and arenes by palladium(II) salts has been published.[10] The present paper deals with the oxidative coupling between aromatic heterocycles and arenes.

Usually arylfurans and -thiophenes and *C*-arylpyrroles and -indoles have been prepared by ring-synthesis. On the other hand, arenediazonium salts are decomposed in a large excess of furans and thiophenes to give α-arylfurans and -thiophenes, respectively.[11] However, no report of direct β-arylation of furans and thiophenes has been published, although β-arylfurans and -thiophenes have been prepared from β-bromofurans[12] and -thiophenes,[13] respectively. We have now found that treatment of furans and thiophenes bearing 2-formyl and 2-acetyl substituents with arenes and palladium(II) acetate gave the corresponding 4-aryl-substituted furans and thiophenes together with small amounts of the 5-aryl-substituted furans and thiophens. On the other hand, treatment of 1-benzoylpyrroles and 1-acetylindoles with arenes and palladium(II) acetate gave the corresponding 2-aryl-substituted pyrroles and indoles. Hardly any reports of direct C-arylation of pyrroles and indoles have, to our knowledge, been published.

Scheme I



Results and Discussions

Attempted oxidative cross-coupling between simple aromatic heterocycles such as furan, 2-methylfuran, thiophene, 2-methylthiophene, 1-methylpyrrole, 1-acetylpyrrole, and 1-methylindole and benzene was unsuccessful, e.g., oxidation of thiophene by palladium acetate in acetic acid which contained benzene at reflux temperature gave a mixture of 2,2′- and 2,3′-bithienyls but none of the phenylthiophenes. On the other hand, oxidation of furfural (**1**) by palladium acetate in acetic acid which contained benzene at reflux temperature gave 2-formyl-4-phenylfuran (**5a**) as a main product, together with 2-formyl-5-phenylfuran (**9a**) and biphenyl (**17**). Treatment of **1** with palladium acetate in a mixture of acetic acid and *p*-dichlorobenzene gave **5b**, **9b**, and 5,5′-diformyl-2,2′-bifuryl (**13**) and in a mixture of acetic acid and *p*-difluorobenzene gave **5c**, **9c**, and **13**. Under similar conditions, reaction of 2-acetylfuran (**2**) with *p*-dichlorobenzene gave 2-acetyl-4-(2,5-dichlorophenyl)furan (**6b**), 2-acetyl-5-(2,5-dichlorophenyl)furan (**10b**), and 5,5′-diacetyl-2,2′-bifuryl (**14**). Furthermore, treatment of 2-formylthiophene (**3**) with palladium acetate in a mixture of acetic acid and benzene gave 2-formyl-4-phenylthiophene (**7a**), 2-formyl-5-phenylthiophene (**11a**), 5,5′-diformyl-2,2′-bithienyl (**15**), and **17**, and the reaction of 2-acetylthiophene (**4**) gave 2-acetyl-4-phenylthiophene (**8a**), 2-acetyl-5-phenylthiophene (**12a**), 5,5′-diacetyl-2,2′-bithienyl (**16**), and **17**. These results are summarized in Table I.

5-8 | **9-12** | **13-16**

5a, 9a, X = O; R = CHO; Ar = C_6H_5
5b, 9b, X = O; R = CHO; Ar = 2,5-$Cl_2C_6H_3$
5c, 9c, X = O; R = CHO; Ar = 2,5-$F_2C_6H_3$
6b, 10b, X = O; R = COMe; Ar = 2,5-$Cl_2C_6H_3$
7a, 11a, X = S; R = CHO; Ar = C_6H_5
8a, 12a, X = S; R = COMe; Ar = C_6H_5

13, X = O; R = CHO
14, X = O; R = COMe
15, X = S; R = CHO
16, X = S; R = COMe

Generally it is known that reaction at the β-position of furan and thiophene rings is not easy. The arylation of **1**, **2**, **3**, and **4** with palladium acetate and arenes is, therefore, of interest as an unusual substitution at the

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Table I. Arylation of Furans and Thiophenes 1, 2, 3, and 4 with Palladium Acetate and Arenes[a]

substrate (mmol[b])	$Pd(OAc)_2$, mmol	arenes	AcOH, mL	reaction time, h	products (isolated yields,[c] %)
1 (3)	1	C_6H_6 (20 mL)	20	7	**5a** (48); **9a** (23); **17** (4)
1 (1)	1	C_6H_6 (20 mL)	20	7	**5a** (15); **9a** (8); **17** (6)
1 (3)	1	p-$Cl_2C_6H_4$ (25 g)	15	7	**5b** (20); **9b** (13); **13** (5)
1 (3)	1	p-$F_2C_6H_4$ (10 mL)	20	7	**5c** (16); **9c** (12); **13** (5)
2 (2)	1	p-$Cl_2C_6H_4$ (22 g)	20	13	**6b** (24); **10b** (15); **14** (7)
3 (15)	4.46	C_6H_6 (50 mL)	50	17	**7a** (30); **11a** (5); **15** (16); **17** (2)
4 (15)	4.46	C_6H_6 (50 mL)	50	17	**8a** (30); **12a** (4); **16** (18); **17** (2)

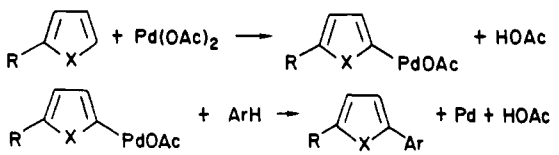
[a] All reactions were performed at reflux temperature under nitrogen. [b] Amounts of the substrates 1, 2, 3, and 4 recovered were not determined. [c] Yields based on palladium acetate used.

Table II. Arylation of 1-Acylpyrroles and 1-Acylindoles 18, 20, 27, and 29 with Palladium Acetate and Arenes[a]

substrate (1 mmol)	$Pd(OAc)_2$, mmol	arenes	AcOH, mL	conv,[b] %	products, (isolated yields,[c] %)
18	1	C_6H_6 (25 mL)	25	88	**19a** (25); **25a** (20); **26** (8)
18	1	p-$Cl_2C_6H_4$ (10 g)	40	90	**25b** (15); **26** (18)
18	1	p-$Me_2C_6H_4$ (25 mL)	25	90	**25d** (28); **26** (12)
20	1.5	C_6H_6 (25 mL)	25	83	**21a** (81)
20	1	p-$Cl_2C_6H_4$ (10 g)	40	70	**22b** (30)
20	1	p-$Me_2C_6H_4$ (25 mL)	25	72	**21d** (36)[d]; **22d** (12)[d]
27	1	C_6H_6 (25 mL)	25	77	**28a** (22)
27	1	p-$Me_2C_6H_4$ (25 mL)	25	76	**28d** (10)
29	1	C_6H_6 (25 mL)	25	50	**30a** (48)

[a] All reactions performed at reflux temperature under nitrogen for 14 h. [b] Conversion of the substrates 18, 20, 27, and 29. [c] Yields based on the substrates 18, 20, 27, and 29 consumed. [d] Yields determined by ^1H NMR spectroscopy.

Scheme II

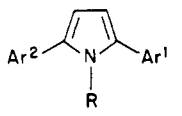


β-position of furan and thiophene rings. Treatment of 5-arylfurans **9a**, **9b**, and **10b** with palladium acetate in acetic acid which contained benzene at reflux temperature did not give the corresponding 4-arylfurans **5a**, **5b**, and **6b**. Under similar conditions, 5-arylfurans **9a**, **9b**, and **10b** were also not obtained from 4-arylfurans **5a**, **5b**, and **6b**. These results eliminated the possibility of rearrangement of both from 4-arylfurans to 5-arylfurans and from 5-arylfurans to 4-arylfurans.

Fujiwara et al.[14] reported that the reaction of furan and of thiophene with palladium acetate and olefins gave 2-alkenyl-substituted furans and thiophenes, respectively. The reaction of **1** and of **3** also resulted in the 5-alkenylation of **1** and of **3**, respectively.[15] These results suggest that palladation to furan and thiophene rings occurred at the α-position. Therefore, the 4-arylation of **1**, **2**, **3**, and **4** by palladium acetate and arenes is explained as reaction between arylpalladium intermediates and aromatic heterocycles (Scheme I), whereas 5-aryl-substituted products are formed via furyl- and thienylpalladium intermediates, as shown in Scheme II.

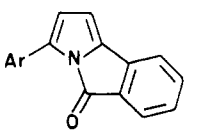
We previously reported the dimerization of 1-benzoylpyrroles[8] and the intramolecular arylation of 1-benzoylindoles[16] by palladium acetate. Intermolecular arylation of 1-acrylpyrroles and -indoles with palladium acetate and arenes were further investigated. The oxidation of 1-benzoylpyrrole (**18**) with palladium acetate in acetic acid which contained benzene gave expected products, 2-phenylpyrroles **19a** and **25a**, together with small amounts of the 2,2'-dimeric compound **26**.[8] However, the treatment of **18** with palladium acetate in a mixture of acetic acid and p-dichlorobenzene and in a mixture of acetic acid and p-xylene gave ring-closed products **25b** and **25d**, respectively, but contrary to our expectation no other arylated products were obtained.

In order to avoid the ring-closure,[17,18] the arylation of 1-(2,6-dichlorobenzoyl)pyrrole (**20**)[18] was investigated. Treatment of **20** with palladium acetate in acetic acid containing benzene gave an expected compound (**21a**) in good yield. Similar reaction of **20** in a mixture of acetic acid and p-dichlorobenzene gave **22b** and in a mixture of acetic acid and p-xylene gave **21d** and **22d**. These results are summarized in Table II.



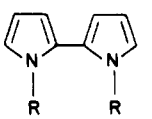
18-24

18, R = C_6H_5CO; Ar^1 = H; Ar^2 = H
19a, R = C_6H_5CO; Ar^1 = C_6H_5; Ar^2 = C_6H_5
20, R = 2,6-$Cl_2C_6H_3CO$; Ar^1 = H; Ar^2 = H
21a, R = 2,6-$Cl_2C_6H_3CO$; Ar^1 = C_6H_5; Ar^2 = C_6H_5
21d, R = 2,6-$Cl_2C_6H_3CO$; Ar^1 = 2,5-$Me_2C_6H_3$; Ar^2 = 2,5-$Me_2C_6H_3$
22b, R = 2,6-$Cl_2C_6H_3CO$; Ar^1 = 2,5-$Cl_2C_6H_3$; Ar^2 = H
22d, R = 2,6-$Cl_2C_6H_3CO$; Ar^1 = 2,5-$Me_2C_6H_3$; Ar^2 = H
23a, R = H; Ar^1 = C_6H_5; Ar^2 = C_6H_5
24b, R = H; Ar^1 = 2,5-$Cl_2C_6H_3$; Ar^2 = H



25

25a, Ar = C_6H_5
25b, Ar = 2,5-$Cl_2C_6H_3$
25d, Ar = 2,5-$Me_2C_6H_3$



26, R = C_6H_5CO

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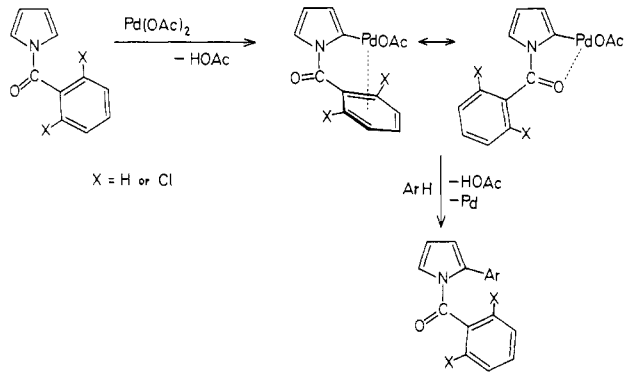
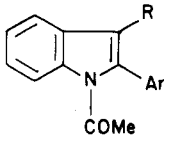
Scheme III



Proton NMR spectra suggest that the products from **18** and **20** are α-aryl-substituted 1-benzoylpyrroles but not β-aryl-substituted compounds. Furthermore, hydrolysis of **19a** and of **22b** gave 2,5-diphenyl-1*H*-pyrrole (**23a**) and 2-(2,5-dichlorophenyl)-1*H*-pyrrole (**24b**), respectively, providing additional evidence for the structures of **19a** and **22b**. It is interesting that the reaction of **18** and **20** with palladium acetate and arenes resulted in the α-arylation of the pyrrole rings, while the arylation of **1**, **2**, **3**, and **4** preferentially occured at the β-position of furan and thiophene rings. This suggests that the arylation of **18** and **20** is explained in terms of formation of (α-pyrrolyl)palladium intermediates which may be stabilized by chelate formation with the benzoyl groups of the intermediates (Scheme III).

Treatment of 1-benzoylindole with palladium acetate in acetic acid which contained benzene gave a ring-closed compound[16] but no phenylated products were obtained. Furthermore, no reaction occurred in the case of 1-(2,6-dichlorobenzoyl)indole.[17] On the other hand, oxidation of 1-acetylindole (**27**) by palladium acetate in acetic acid which contained benzene gave 1-acetyl-2-phenylindole (**28a**). The arylation of **27** with *p*-xylene gave **28d**. Under similar conditions, 1-acetyl-3-methylindole (**29**) reacted with palladium acetate and benzene to give **30a**.

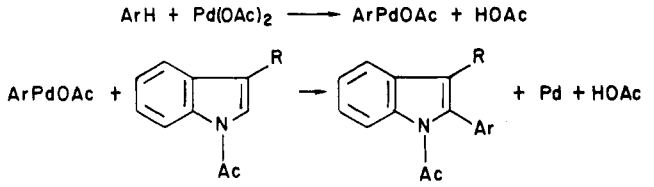


27, R = H; Ar = H
28a, R = H; Ar = C_6H_5
28d, R = H; Ar = 2,5-$Me_2C_6H_3$
29, R = Me; Ar = H
30a, R = Me; Ar = C_6H_5

Proton NMR spectra suggest that the structure of **28a** and **28d** are 2-arylindoles but not 3-arylindoles. Also, hydrolysis of **28a** gave 2-phenyl-1*H*-indole (**31a**), providing additional evidence for the structure of **28a**. Previously we reported that the palladation of 1-acylindoles occurred at the 3-position but not the 2-position of the indole ring.[19] Therefore, Scheme IV is derived for the 2-arylation of **27** with palladium acetate and arenes.

The oxidative coupling between aromatic heterocycles and arenes by palladium acetate provides an easy and effective method for preparation of aryl-substituted aromatic heterocycles. The reaction will be further extended to cross-coupling of different aromatic heterocycles, although Kozhevnikov[20] already reported the cross-coupling between furans and thiophenes.

Scheme IV



Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Proton magnetic resonance spectra were obtained with a JEOL PMX60A spectrometer with tetramethylsilane as an internal standard. Infrared spectra were measured with a JASCO IRA-1 spectrometer. Mass spectra were obtained with a JEOL JMS-D300 spectrometer. The elemental analyses were performed by the Analytical Center of Kyoto University. Preparative thin-layer chromatography was performed with Merck silica gel GF-254 or Wako silica gel B-5F. Furfural (**1**), 2-acetylfuran (**2**), 2-formylthiophene (**3**), and 2-acetylthiophene (**4**) were obtained commercially. 1-Benzoylpyrrole (**18**), 1-(2,6-dichlorobenzoyl)pyrrole (**20**), 1-acetylindole (**27**), and 1-acetyl-3-methylindole (**29**) were prepared according to the procedure described before.[17,18]

General Procedure for Arylation of Aromatic Heterocycles with Arenes and Palladium Acetate. A solution of aromatic heterocycles and palladium acetate in acetic acid which contained arenes was heated at reflux temperature under nitrogen. The reaction mixture was evaporated to give a residue which was then chromatographed by silica gel TLC, developed with benzene, to give aryl-substituted aromatic heterocycles. These results are summarized in Table I and Table II. The spectral and analytical data of the products are given below.

2-Formyl-4-phenylfuran (5a): bp 135 °C (3 torr); NMR ($CDCl_3$) δ 7.2–7.6 (m, 6 H), 7.90 (s, 1 H), 9.66 (s, 1 H); IR (film) 1680 cm^{-1}; mass spectrum, *m/e* (relative intensity) 173 (13), 172 (100), 171 (36), 115 (88). Anal. Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.69; H, 4.64.

2-Formyl-4-(2,5-dichlorophenyl)furan (5b): mp 129–129.5 °C; NMR ($CDCl_3$) δ 7.23–7.5 (m, 3 H), 7.51 (s, 1 H), 8.01 (s, 1 H), 9.69 (s, 1 H); IR (Nujol) 1685 cm^{-1}; mass spectrum, *m/e* (relative intensity) 242 (58), 241 (45), 240 (100), 239 (55), 185 (28), 183 (44). Anal. Calcd for $C_{11}H_6O_2Cl_2$: C, 54.81; H, 2.51. Found: C, 54.99; H, 2.78.

2-Formyl-4-(2,5-difluorophenyl)furan (5c): mp 87–88 °C; NMR ($CDCl_3$) δ 6.9–7.4 (m, 3 H), 7.51 (s, 1 H), 8.10 (s, 1 H), 9.69 (s, 1 H); IR (Nujol) 1685 cm^{-1}: mass spectrum, *m/e* (relative intensity) 209 (13), 208 (100), 207 (72), 152 (7), 151 (63). Anal. Calcd for $C_{11}H_6O_2F_2$: C, 63.47; H, 2.91. Found: C, 63.18; H, 2.77.

2-Acetyl-4-(2,5-dichlorophenyl)furan (6b): mp 125–126.5 °C; NMR ($CDCl_3$) δ 2.51 (s, 3 H), 7.23–7.5 (m, 3 H), 7.46 (s, 1 H), 7.91 (s, 1 H); IR (Nujol) 1670 cm^{-1}; mass spectrum, *m/e* (relative intensity) 256 (35), 254 (53), 241 (64), 239 (100). Anal. Calcd for $C_{12}H_8O_2Cl_2$: C, 56.50; H, 3.16. Found: C, 56.39; H, 3.03.

2-Formyl-4-phenylthiophene (7a): mp 67.5–68.5 °C (lit.[21] mp 67–68 °C, lit.[22] mp 56–57 °C); NMR ($CDCl_3$) δ 7.24–7.68 (m, 5 H), 7.83 (d, d, 1 H, J = 1.5, 1 Hz), 8.02 (d, 1 H, J = 1.5 Hz), 9.97 (d, 1 H, J = 1 Hz); IR (Nujol) 1670 cm^{-1}.

2-Acetyl-4-phenylthiophene (8a): mp 59–60 °C (lit.[21] mp 56–57 °C); NMR ($CDCl_3$) δ 2.58 (s, 3 H), 7.23–7.67 (m, 5 H), 7.71 (d, 1 H, J = 2 Hz), 7.94 (d, 1 H, J = 2 Hz); IR (Nujol) 1670 cm^{-1}.

2-Formyl-5-phenylfuran (9a): bp 145 °C (5 torr) (lit.[23] bp 146 °C (5 torr)); NMR ($CDCl_3$) δ 6.77 (d, 1 H, J = 4 Hz), 7.2–7.5 (m, 4 H), 7.66–7.9 (m, 2 H), 9.57 (s, 1 H); IR (film) 1670 cm^{-1}; mass spectrum, *m/e* (relative intensity) 172 (81), 171 (29), 116 (17), 115 (100).

2-Formyl-5-(2,5-dichlorophenyl)furan (9b): mp 100–101 °C; NMR ($CDCl_3$) δ 7.2–7.4 (m, 4 H), 7.97 (d, 1 H, J = 3 Hz), 9.66

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(s, 1 H); IR (Nujol) 1680 cm^{-1}; mass spectrum, *m/e* (relative intensity) 242 (66), 241 (32), 240 (100), 239 (37), 185 (38), 183 (54). Anal. Calcd for $C_{11}H_6O_2Cl_2$: C, 54.81; H, 2.51. Found: C, 54.83; H, 2.55.

2-Formyl-5-(2,5-difluorophenyl)furan (9c): mp 93.5–94.5 °C; NMR ($CDCl_3$) δ 7.00 (d, 1 H, J = 4 Hz), 7.32 (d, 1 H, J = 4 Hz), 6.95–7.35 (m, 2 H), 7.5–7.83 (m, 1 H) 9.66 (s, 1 H); IR (Nujol) 1675 cm^{-1}; mass spectrum, *m/e* (relative intensity) 209 (12), 208 (100), 207 (55), 152 (13), 151 (94). Anal. Calcd for $C_{11}H_6O_2F_2$: C, 63.47; H, 2.91. Found: C, 63.19; H, 2.93.

2-Acetyl-5-(2,5-dichlorophenyl)furan (10b): mp 100–101 °C; NMR ($CDCl_3$) δ 2.53 (s, 3 H), 7.15–7.3 (m, 3 H), 7.29 (d, 1 H, J = 3 Hz), 7.89 (d, 1 H, J = 3 Hz); IR (Nujol) 1680 cm^{-1}; mass spectrum, *m/e* (relative intensity) 256 (46), 254 (71), 241 (71), 239 (100). Anal. Calcd for $C_{12}H_8O_2Cl_2$: C, 56.50; H, 3.16. Found: C, 56.23; H, 3.06.

2-Formyl-5-phenylthiophene (11a): mp 93–94 °C (lit.[24] mp 93–93.5 °C); NMR ($CDCl_3$) δ 7.37 (d, 1 H, J = 4 Hz), 7.71 (d, 1 H, J = 4 Hz), 7.3–7.8 (m, 5 H), 9.85 (s, 1 H); IR (Nujol) 1660 cm^{-1}.

2-Acetyl-5-phenylthiophene (12a): mp 114.5–116 °C (lit.[24] mp 113–115 °C); NMR ($CDCl_3$) δ 2.55 (s, 3 H), 7.27 (d, 1 H, J = 4 Hz), 7.62 (d, 1 H, J = 4 Hz), 7.2–7.75 (sm, 5 H); IR (Nujol) 1650 cm^{-1}.

1-Benzoyl-2,5-diphenylpyrrole (19a): mp 153–154 °C; NMR ($CDCl_3$) δ 6.43 (s, 2 H), 7.06–7.56 (m, 15 H); IR (Nujol) 1710 cm^{-1}; mass spectrum, *m/e* (relative intensity) 323 (13), 105 (100), 77 (36). Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.52; H, 5.27; N, 4.18.

1-(2,6-Dichlorobenzoyl)-2,5-diphenylpyrrole (21a): mp 137–138 °C; NMR ($CDCl_3$) δ 6.28 (s, 2 H), 6.89 (s, 3 H), 7.1–7.53 (m, 10 H); IR (Nujol) 1710 cm^{-1}: mass spectrum, *m/e* (relative intensity) 393 (10), 391 (16), 175 (68), 173 (100). Anal. Calcd for $C_{23}H_{15}NOCl_2$: C, 70.42; H, 3.85; N, 3.57. Found: C, 70.29; H, 3.88; N, 3.44.

1-(2,6-Dichlorobenzoyl)-2,5-bis(2,5-dimethylphenyl)pyrrole (21d): mp 122–123 °C; NMR ($CDCl_3$) δ 2.20 (s, 6 H), 2.28 (s, 6 H), 6.18 (s, 2 H), 6.85–7.25 (m, 9 H); IR (Nujol) 1710 cm^{-1}; mass spectrum, *m/e* (relative intensity) 449 (23), 447 (38), 274 (30), 175 (65), 173 (100). Anal. Calcd for $C_{27}H_{23}NOCl_2$: C, 72.32; H, 5.17; N, 3.12. Found: C, 72.55; H, 5.24; N, 2.98.

1-(2,6-Dichlorobenzoyl)-2-(2,5-dichlorophenyl)pyrrole (22b): mp 160–162 °C: NMR ($CDCl_3$) δ 6.27–6.44 (m, 2 H), 6.55–6.77 (m, 1 H), 7.1–7.5 (m, 6 H); IR (Nujol) 1710 cm^{-1}; mass spectrum, *m/e* (relative intensity) 385 (4), 383 (3), 350 (17), 348 (18), 177 (11), 176 (6), 175 (67), 173 (100). Anal. Calcd for $C_{17}H_9NOCl_4$: C, 53.02; H, 2.36; N, 3.64. Found: C, 52.75; H, 2.43; N, 3.58.

1-(2,6-Dichlorobenzoyl)-2-(2,5-dimethylphenyl)pyrrole (22d): mp 114–115 °C; NMR ($CDCl_3$) δ 2.19 (br, 6 H), 6.1–6.4 (m, 2 H), 6.4–7.4 (m, 7 H); IR (Nujol) 1710 cm^{-1}; mass spectrum, *m/e* (relative intensity) 345 (16), 343 (25), 177 (11), 175 (66), 173 (100). Anal. Calcd for $C_{19}H_{15}NOCl_2$: C, 66.29; H, 4.39; N, 4.07. Found: C, 66.37; H, 4.21; N, 4.04.

3-Phenyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (25a): mp 114.5–115.5 °C; NMR ($CDCl_3$) δ 6.24 (s, 2 H), 7.06–7.9 (m, 9 H); IR (Nujol) 1740 cm^{-1}; mass spectrum, *m/e* (relative intensity) 246 (19), 245 (100), 216 (15), 114 (15). Anal. Calcd for $C_{17}H_{11}NO$: C, 83.24; H, 4.52; N, 5.71. Found: C, 83.40; H, 4.66; N, 5.54.

3-(2,5-Dichlorophenyl)-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (25b): mp 170–171 °C; NMR ($CDCl_3$) δ 6.28 (s, 2 H), 7.1–7.76 (m, 7 H); IR (Nujol) 1755 cm^{-1}; mass spectrum, *m/e* (relative intensity) 315 (30), 313 (45), 280 (34), 279 (20), 278 (100), 214 (11), 139 (12). Anal. Calcd for $C_{17}H_9NOCl_2$: C, 64.99; H, 2.89; N, 4.46. Found: C, 65.27, H, 2.86; N, 4.47.

3-(2,5-Dimethylphenyl)-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (25d): mp 99–100 °C; NMR ($CDCl_3$) δ 2.31 (br, 6 H), 6.03 (d, 1 H, J = 3 Hz), 6.26 (d, 1 H, J = 3 Hz), 6.95–7.7 (m, 7 H); IR (Nujol) 1740 cm^{-1}; mass spectrum, *m/e* (relative intensity) 274 (22), 273 (100), 272 (16), 256 (12), 115 (11). Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.22; H, 5.73; N, 5.05.

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1,1′-Dibenzoyl-2,2′-bipyrrole (26): mp 150–151 °C; NMR ($CDCl_3$) δ 6.26 (t, 2 H, J = 3 Hz), 6.4–6.53 (m, 2 H), 6.87–7.0 (m, 2 H), 7.23–7.83 (m, 10 H); IR (Nujol) 1700 cm^{-1}; mass spectrum, *m/e* (relative intensity) 341 (7), 340 (29), 338 (8), 106 (8), 105 (100), 77 (28). Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.68; H, 5.01; N, 8.25.

1-Acetyl-2-phenylindole (28a): bp 200 °C (8 torr); NMR ($CDCl_3$) δ 1.96 (s, 3 H), 6.63 (s, 1 H), 7.2–7.7 (m, 8 H), 8.33–8.53 (m, 1 H); IR (film) 1705 cm^{-1}; mass spectrum, *m/e* (relative intensity) 236 (12), 235 (64), 221 (10), 194 (54), 193 (100), 192 (24), 191 (14), 190 (11), 171 (18), 165 (50), 105 (80). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.41; H, 5.77; N, 5.98.

1-Acetyl-2-(2,5-dimethylphenyl)indole (28d): mp 107–108 °C; NMR ($CDCl_3$) δ 1.94 (s, 3 H), 2.16 (s, 3 H), 2.35 (s, 3 H), 6.48 (s, 1 H), 7.1–7.65 (m, 6 H), 8.33–8.56 (m, 1 H); IR (Nujol) 1705 cm^{-1}; mass spectrum, *m/e* (relative intensity) 264 (13), 263 (61), 222 (18), 221 (100), 220 (25), 204 (15). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 81.95; H, 6.56; N, 5.21.

1-Acetyl-3-methyl-2-phenylindole (30a): mp 80.5–81.5 °C; NMR ($CDCl_3$) δ 1.95 (s, 3 H), 2.13 (s, 3 H), 7.23–7.63 (m, 8 H), 8.33–8.55 (m, 1 H); mass spectrum, *m/e* (relative intensity) 250 (8), 249 (40), 208 (16), 207 (100), 206 (57), 205 (7), 204 (16), 130 (18), 128 (11). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.91; H, 5.94; N, 5.44.

5,5′-Diformyl-2,2′-bifuryl (**13**), 5,5′-diacetyl-2,2′-bifuryl (**14**), 5,5′-diformyl-2,2′-bithienyl (**15**), and 5,5′-diacetyl-2,2′-bithienyl (**16**) were identified by comparison with authentic samples.[6]

Hydrolysis of Aryl-Substituted 1-Acylpyrroles 19a and 22b and of 1-Acetyl-2-phenylindole (28a). A solution of **19a** (70 mg) in 2:1 ethanol/3 N sodium hydroxide (120 mL) was heated at reflux temperature for 7 h. The mixture was carefully neutralized with dilute hydrochloric acid and extracted with chloroform. The extract was evaporated to give a residue which was chromatographed by silica gel TLC, developed with benzene, to give **19a** recovered (33 mg) and 2,5-diphenyl-1*H*-pyrrole (**23a**), mp 142–144 °C (lit.[25] mp 143–144 °C) (14 mg), 55% yield based on **19a** consumed.

Similar treatment of **22b** (70 mg) gave **22b** recovered (26 mg) and 2-(2,5-dichlorophenyl)-1*H*-pyrrole (**24b**) (15 mg), 62% yield based on **22b** consumed: mp 109–109.5 °C; NMR ($CDCl_3$) δ 6.23–6.43 (m, 1 H), 6.56–6.73 (m, 1 H), 6.86–7.06 (m, 1 H), 7.22 (d, d, 1 H, J = 9, 2 Hz), 7.34 (d, 1 H, J = 9 Hz), 7.54 (d, 1 H, J = 2 Hz), 9.0 (br, 1 H); IR (Nujol) 3350 cm^{-1}; mass spectrum, *m/e* (relative intensity) 213 (66), 211 (100), 176 (15), 149 (31), 141 (13). Anal. Calcd for $C_{10}H_7NCl_2$: C, 56.63; H, 3.33; N, 6.60. Found: C, 57.05; H, 3.49; N, 6.68.

Similar treatment of **28a** (50 mg) in 2:1 ethanol/3 N sodium hydroxide (60 mL) at 70 °C for 1 h gave **28a** recovered (11 mg) and 2-phenyl-1*H*-indole (**31a**) (30 mg), 95% yield based on **28a** consumed. The product **31a** was identified by comparison with the authentic sample obtained commercially.

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Registry No. 1, 98-01-1; **2**, 1192-62-7; **3**, 98-03-3; **4**, 88-15-3; **5a**, 99113-85-6; **5b**, 99113-86-7; **5c**, 99113-87-8; **6b**, 99113-88-9; **7a**, 26170-87-6; **8a**, 26170-93-4; **9a**, 13803-39-9; **9b**, 99113-89-0; **9c**, 99113-90-3; **10b**, 99113-91-4; **11a**, 19163-21-4; **12a**, 1665-41-4; **13**, 5905-01-1; **14**, 91544-08-0; **15**, 32364-72-0; **16**, 18494-73-0; **17**, 92-52-4; **18**, 5145-65-3; **19a**, 78388-83-7; **20**, 78388-82-6; **21a**, 78388-87-1; **21d**, 78388-88-2; **22b**, 78388-90-6; **22d**, 78388-89-3; **23a**, 838-40-4; **24b**, 99113-94-7; **25a**, 78388-84-8; **25b**, 78388-86-0; **25d**, 99113-92-5; **26**, 74117-41-2; **27**, 576-15-8; **28a**, 78388-91-7; **28d**, 99113-93-6; **29**, 23543-66-0; **30a**, 78388-92-8; **31a**, 948-65-2; C_6H_6, 71-43-2; *p*-$Cl_2C_6H_4$, 106-46-7; *p*-$F_2C_6H_4$, 540-36-3; $Pd(OAc)_2$, 3375-31-3; *p*-$Me_2C_6H_4$, 106-42-3.

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