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Oxidation of Pyrroles with Benzoyl Peroxide: Synthesis of Mono- and Dihydroxypyrrole O-Benzoates and Oxidative Cleavage of Pyrrole-2-methanols*,[1,2]

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Benzoyl peroxide converts pyrroles into 2-hydroxy- and 2,5-dihydroxy O-benzoates. The mono- and di-O-benzoates of N-substituted pyrroles were prepared by this convenient one-step procedure. The mechanism was discussed in terms of both homolytic and heterolytic factors, and general aspects of homolytic substitution of the pyrrole ring were also discussed in comparison with other five-membered heterocycles. On treatment with benzoyl peroxide N-substituted pyrrole-2-methanols undergo novel C-C cleavage to give the O-benzoates.

In the last two decades arylation has been the most studied homolytic aromatic substitution, also in the heteroaromatic series.[4,5] The general characteristics of the reactions are substantially the same as those observed in the homocyclic aromatic series, for which comprehensive reviews are available.[6] Among the usual sources used for the homolytic arylation there seems to be a notable difference in behavior between aroyl peroxides and other reagents as discussed below.

Thermolysis of benzoyl peroxide **1** ($(BzO)_2$; Bz=benzoyl)[6,7] yields two benzoyloxy radicals **2**, some of which, by loss of carbon dioxide, yield phenyl radicals **3** which participate in the phenylation, usually by way of a σ-complex **5** with radical character, to give phenyl products **7**. Alternatively, benzoyloxy radicals **2** may also react with aromatic substrates to give esters by way of a related σ-complex **4**, which loses a hydrogen atom in the presence of appropriate hydrogen acceptors to form benzoyloxy products **6**. Usually phenylation to **7** is a major reaction accompanied by benzoyloxylation to **6** as a side reaction. Benzoyloxylation increases with the "reactivity" of the aromatic substrates.[6] Although benzoyloxylation with **1** is only a minor reaction ($<10\%$) with benzene derivatives unless electron-donating substituents are present, the more reactive substrates such as methoxyl-substituted or polynuclear aromatics undergo predominantly benzoyloxylation.[8] This dual functionality toward phenylation and benzoyloxylation is characteristic of **1** and render a special synthetic possibility to the reagent.

Heteroaromatics are classified into two major categories: the π-electron-deficient system and the π-electron excessive system.[9] The simplest examples of one-nitrogen series for these

* Dedicated to the memory of Prof. Eiji Ochiai.

1) Reactions of Heteroaromatics and Aromatics with Benzoyl Peroxide V. Part IV: M. Aiura and Y. Kanaoka, *Heterocycles*, **2**, 319 (1974).
2) Preliminary communication: M. Aiura and Y. Kanaoka, *Heterocycles*, **1**, 237 (1973).
3) Location: *Kita-12 Nishi-6, Kita-ku, Sapporo, 060, Japan.*
4) R.O.C. Norman and G.K. Radda, "Advances in Heterocyclic Chemistry," Vol. 2, A.R. Katritzky, A.J. Boulton ed., Academic Press, New York, 1963, p. 131.
5) F. Minisci and O. Porta, "Advances in Heterocyclic Chemistry," Vol. 16, A.R. Katritzky, A.J. Boulton ed., Academic Press, New York, 1974, p. 123.
6) G.H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960, p. 116.
7) W.A. Pryer, "Free Radicales," McGraw-Hill, New York, 1966, p. 253.
8) D.J. Rawlinson and G. Sosnovsky, *Synthesis*, **1972**, 16.
9) A. Albert, "Heterocyclic Chemistry," Athlon, **1959**.

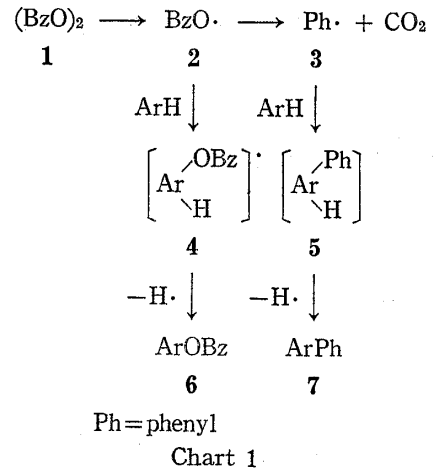


Chart 1

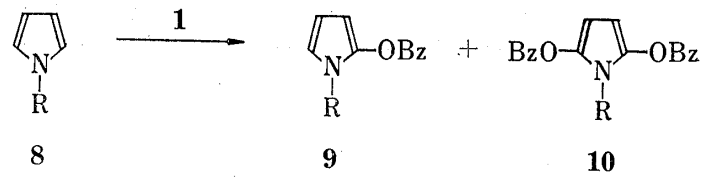


Chart 2

systems are pyridine and pyrrole, respectively. Compounds belonging to the latter series are generally reactive toward electrophilic species and therefore must be suitable for benzoyloxylation with **1**. Namely, in going from the π-electron deficient heteroaromatics to the excessive ones, the reaction pattern of **1** may change from phenylation **7** to benzoyloxylation **6** depending upon the electrophilic reactivity of the substrates. In fact, it has been already shown that reactions of **1** with thiophene[10] and furan[11] take different courses from the normal phenylation. Our previous work further demonstrated that N-methylindoles, the most common one-nitrogen heteroaromatics in the π-electron excessive system, undergo typical benzoyloxylation to lead to the corresponding indoxyl, oxindole and dioxindole O-benzoates.[12] Here we report that the above formulation is now established with pyrrole, the simplest and representative member of the series.

Benzoyloxylation of pyrrole itself was difficult to control giving intractable tar. As in the case of indole,[12] apparently the abstraction of a hydrogen atom from the NH group of pyrrole leads to side reactions. However, N-substituted pyrroles were moderately reactive toward **1** and gave the expected oxygenated products. In a typical experiment, two-fold excess 1-methylpyrrole **8** in benzene solution was allowed to react with **1** at room temperature for 36 hr. After preparative TLC, 2-benzoyloxy-1-methylpyrrole **9a** (27%) and 2,5-dibenzoyloxy-1-methylpyrrole **10a** (30%) were isolated. **9a** had the composition $C_5H_7N+C_7H_5O_2$, *m/e* 201, a 1:1 reaction product, and the structure was supported by the NMR data (CCl_4: δ 5.70—6.00 (2H, m; C_3–H, C_4–H of pyrrole), 6.24 (1H, d—d, J=3 Hz, 2 Hz; C_5–H) and the IR spectrum (1745 cm^{-1}, ester). **10a** was a 1:2 reaction product ($C_5H_6N+2C_7H_5O_2$; *m/e* 321) whose structure was likewise supported by the NMR (δ 5.77 (2H, s; C_3–H, C_4–H)) and the IR (1740 cm^{-1}, ester) data. Neither phenylated pyrroles expected from "normal" homolytic aromatic substitution with **1** nor 3-substituted derivatives were detected in the reaction mixture. The formation of **10a** may be explained by subsequent benzoyloxylation of initially formed **9a**. N-Phenylpyrrole **8c** was less reactive than the N-methyl and benzyl analogs (**8a**, **8b**) and prolonged heating was necessary for the reaction, while *p*-methoxyphenylpyrrole **8d** was more reactive than **8c**. These results are summarized in Table I.

Table I. Yields of Benzoyloxypyrroles (**9**, **10**) from **8**

Substrate **8**	Solvent	Temp. (°C)	Time (hr)	Yields (%) **9**	**10**
a	benzene	room temp.	36	27	30
b	benzene	60	2	24	35
c	acetonitrile	80	18	18	10
d	benzene	60	24	28	8

10) C.E. Griffin and K.R. Martin, *Chem. Comm.*, **1965**, 154.
11) K.E. Kolb and W.A. Black, *Chem. Comm.*, **1969**, 1119.
12) Y. Kanaoka, M. Aiura, and S. Hariya, *J. Org. Chem.*, **36**, 458 (1971).

Whereas homolytic aromatic substitution of five-membered heterocycles such as thiophene[10,13,14] and furan[11,15] has recently received extensive studies, very little is known about the behavior of pyrroles with free radicals. An only example of radical-type reaction of pyrrole is phenylation of N-carbethoxypyrrole with nitrosoacetanilide.[16] The lack of literature may largely be due to too high reactivity of the N–H group of pyrrole for radicals, and this difficulty has now been circumvented in our present work in which N-substituted pyrroles are used as the substrates. A comparison of the reactivities of thiophene, furan and pyrrole, the fundamental series of the π-electron excessive heteroaromatic system, is thus available in terms of their behaviors toward **1** (Chart 3).

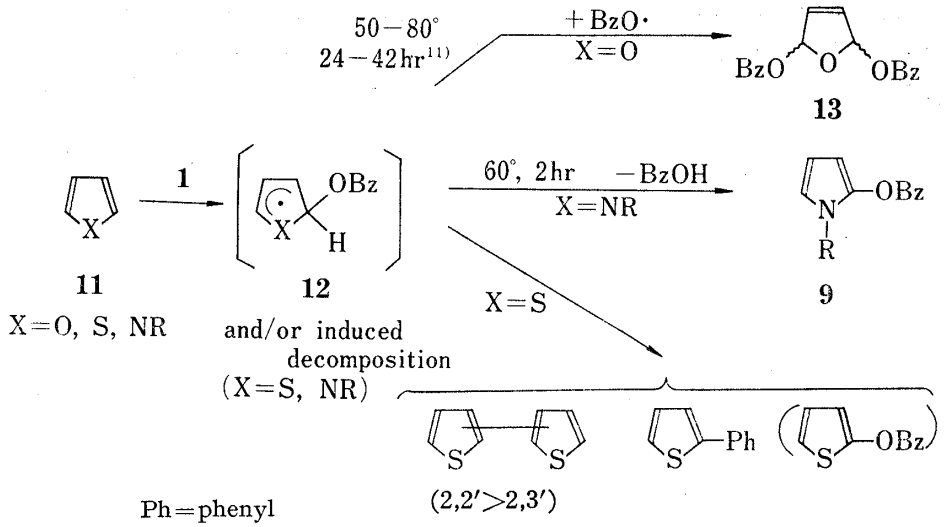


Chart 3

In spite of the diverse patterns of the reaction, one feature common to them is that the 2-position of the rings is invariably the site of attack. It has been established in thiophene and furan that homolytic attack at the 2-position predominates or is exclusive in the case of phenylation.[4,5,14,15] Although there are little experimental data for homolytic substitution of the pyrrole ring,[16] some prediction may be made on the basis of many theoretical studies of the electronic structure of pyrrole using the molecular orbital approach with various degree of refinement.[17–19] Even qualitative comparison of the relative stabilities of resonance forms of the σ-complexes suggests the site of preferential homolytic substitution to be the 2-position. Free valence values, a simple parameter pertinent to homolytic reactivity,[20] are relatively high at the 2-carbon: 1-, 0.623; 2-, 0.453; 3-, 0.404.[21] Frontier electron densities as radical

13) M.C. Ford and D. Mackay, *J. Chem. Soc.*, **1957**, 4620.
14) *a*) C.M. Camaggi, R. Leardini, M. Tiecco, and A. Tundo, *J. Chem. Soc.* (*B*), **1969**, 1251; *b*) *Idem, ibid.*, **1970**, 1683; *c*) P. Spagnolo, L. Testaferri, M. Tiecco, and G. Martelli, *J. Chem. Soc. Perkin I*, **1972**, 93; *d*) P. Spagnolo, M. Tiecco, A. Tundo, and G. Martelli, *ibid., Perkin I*, **1972**, 556; *e*) C.M. Camaggi, G. Deluca, and A. Tundo, *ibid., Perkin II*, **1972**, 412; *f*) E.K. Fields and S. Meyerson, *J. Org. Chem.*, **35**, 67 (1970).
15) *a*) O.C. Ayres and J.R. Smith, *J. Chem. Soc.* (*C*), **1968**, 2737; *b*) L. Benati, N. LaBarba, M. Tiecco, and A. Tundo, *ibid.* (*B*), **1969**, 1253; *c*) C. Benati, M. Tiecco, A. Tundo, and F. Taddei, *ibid.* (*B*), **1970**, 1443.
16) I.J. Rinkes, *Rec. Trav. Chim.*, **62**, 116 (1943).
17) R.A. Jones, "Advances in Heterocyclic Chemistry," Vol. 11, A.R. Katritzky, A.J. Boulton, ed., Academic Press, New York, 1970, p. 383.
18) K. Schofield, "Hetero-Aromatic Nitrogen Compounds," Butterworths, London, **1967**, p. 89.
19) R.L. Miller, P.G. Lykos, and H.N. Schmeising, *J. Am. Chem. Soc.*, **84**, 4623 (1962).
20) A. Streitwieser, "Molecular Orbital Theory," Wiley, New York, 1961, p. 289.
21) R.D. Brown, *Aust. J. Chem.*, **8**, 100 (1955).

reaction indices are: 2-, 0.661; 3-, 0.292.[19] On the other hand, numerous examples have indicated that electrophilic substitution takes place predominantly also at the 2-carbon.[17-19,22,23] Moreover, it is well established that benzoyloxy radicals are of electrophilic nature.[6,7,24] Therefore the regioselective benzoyloxylation at the 2-position of pyrrole is rationalized in terms of the combined homolytic and heterolytic factors as above. As shown in Chart 4, the transition state may be stabilized by the resonance forms (14↔15) in which an electron is transfered from one radical to the other. Induced decomposition of **1**, known to occur in presence of a nucleophile such as an amine,[7,25] may well be involved possibly by way of a path including a radical cation **16** and a pyrrolyl radical **17**, as suggested also in the reaction of thiophene[5,10] (Chart 3). The fact that the reaction can proceed at room temperature is in accord with this inference in view of the life time of **1**.[7] The polar effect can also explain the influence of the N-substituents on their relative reactivities (Table I): Electron-withdrawing phenyl group in **8c** retards the reaction, while this effect is somewhat compensated by the *p*-methoxy group in **8d**.

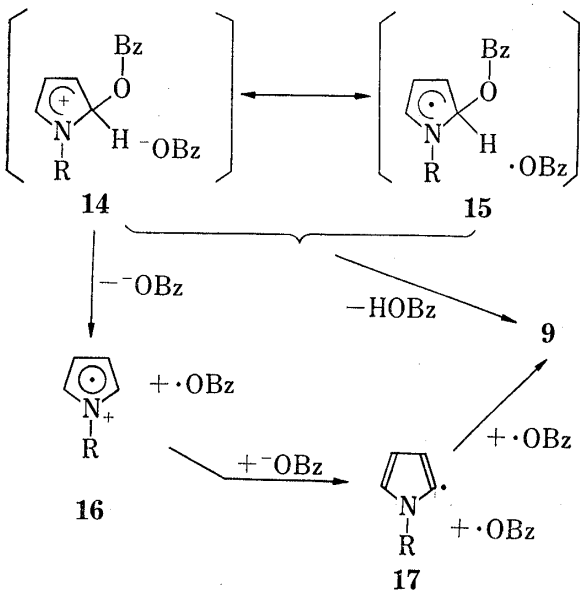
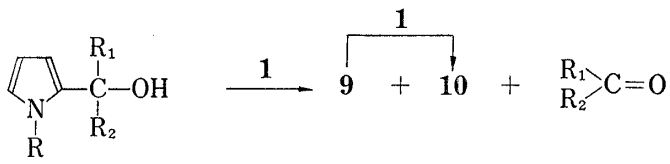


Chart 4



Ph=phenyl

a: R=Me, R_1=R_2=H
b: R=Me, R_1=H, R_2=Ph
c: R=Me, R_1=R_2=Ph
d: R=Ph, R_1=R_2=H

Chart 5

Comparison of the reaction conditions shows that pyrrole is more reactive than furan **11** (X=O)[11] which reacts with a benzoyloxy radical **2** probably along a typical homolytic process *via* σ-complex **12** (Chart 3). That thiophene is least reactive is indicated by the observation that the phenylation is preferred to benzoyloxylation.[26] The reaction order toward **1** is thus pyrrole>furan>thiophene, consistent with previous studies of their homolytic reactions.[4,5,15b,27] Finally, the different behaviors of furan (to give 2,5-dihydro derivatives **13**) and pyrrole are ascribed to the dienic character of furan[5,23] and the aromaticity of pyrrole,[17,18,23] respectively.

In the course of this study, it was observed that N-methylpyrrole-2-methanol **18a**, on treatment with **1**, undergoes unexpected facile cleavage of the C–C bond giving rise to the

22) A.H. Corwin, "Heterocyclic Compounds," Vol. 1, R.C. Elderfield, ed., Wiley, New York, 1950, p. 277.
23) L.A. Paquette, "Principles of Modern Heterocyclic Chemistry," Benjamin Inc., New York, 1968, p. 102.
24) M.E. Kurzand and M. Pellegrini, *J. Org. Chem.*, **25**, 900 (1970).
25) H. Yano, K. Takemoto, and M. Imoto, *J. Macromol. Sci. Chem.* A2 (4), 739 (1968).
26) Benzoyloxylation of thiophene was noted.[13] However, the subsequent paper reported only formation of 2-phenylthiophene and bithienyls.[10]
27) In homolytic phenylation, relative rates of furan and thiophene are 11.5 and 2.6, respectively. Partial rate factors: furan (2-, 34.5; 3-, 0.1); thiophene (2-, 7.3; 3-, 0.5).[4,5,15b]

benzoyloxy derivatives (**9, 10**). Under the mild conditions, **18b—d** were similarly transformed into the mono and/or dibenzoyloxy derivatives demonstrating the generality of this reaction (Table II). Benzaldehyde was identified as the counterpart of the fragmentation in the case of **18b**. This unusual oxidative transformation, probably analogous to the fission of some methanol derivatives with lead tetraacetate,[28] may be characteristic of the pyrrole ring since, for example, furan-2-methanol did not react under similar conditions. Although the mech-

Table II. Yields of Benzoyloxypyrroles (**9, 10**) from **18**

Substrate **18**	Solvent	Temp.°	Time (hr)	Yields (%) **9**	**10**
a	benzene	room temp.	3	7	27
b	benzene	room temp.	2	28	42
c	benzene	room temp.	3	—	56
d	benzene	room temp.	36	19	24

anism is unknown yet, certain ionic character must be considered since the reaction also proceeds at room temperature. Two conceivable pathways are shown in Chart 6. The cyclic path (a) seems less probable in view of that the hydroxyl may not be sufficiently nucleophilic. In the alternative path (b) the driving force would be the attack by the highly nucleophilic 2-carbon to the peroxide oxygen followed by a concerted cleavage of the C–C bond.

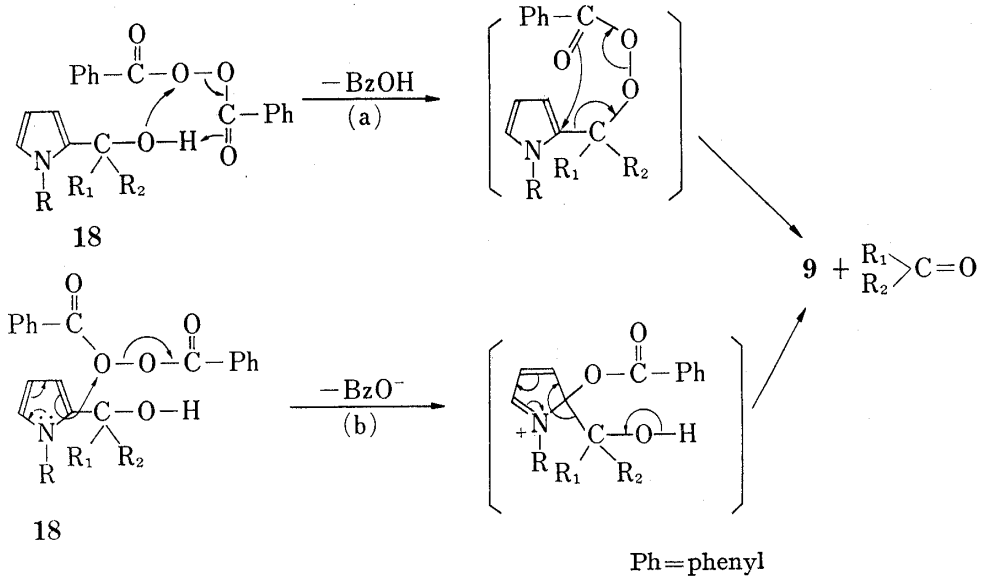


Chart 6

Since N-substituted pyrroles are shown to be suitable substrates for reactions with homolytic species, this may open a new field of radical chemistry of pyrroles. The benzoyloxylation affords a simple one-step method for preparation of oxygenated pyrroles. In addition, the products (**9,10**) are found to be interesting synthetic substrates, for example, in the Diels-Alder reaction, due to activation of the pyrrole ring by the benzoyloxy substituent. This synthetic application will be reported separately.

28) *a*) W.A. Mosher and H.A. Neidig, *J. Am. Chem. Soc.*, **72**, 4452 (1950); *b*) W.A. Mosher, C.L. Kehr, and L.W. Wright, *J. Org. Chem.*, **26**, 1044 (1961).

Experimental[29]

Reaction of 1-Methylpyrrole 8a with Benzoyl Peroxide——**1** (1.21 g, 5 mmoles) was added to a solution of **8a** (810 mg, 10 mmoles) in benzene (6 ml) and the solution was allowed to stand at room temperature for 36 hr. The mixture was washed with saturated aq. $NaHCO_3$ and then water to remove benzoic acid formed, dried (Na_2SO_4) and evaporated *in vacuo*. The residue was subjected to TLC (ether: hexane=1: 5) to give **9a** (270 mg, 27%) and **10a** (240 mg, 30%).

2-Benzoyloxy-1-methylpyrrole **9a**: Colorless prisms from hexane, mp 42—43°, UV λ_{max}^{EtOH} nm (log ε): 229 (3.85), 268 (3.3), 275 (3.3), 290 (3.27). IR ν_{max}^{Nujol} cm^{-1}: 1745. Mass Spectrum *m/e*: 201 (M^+). NMR (CCl_4), δ: 3.47 (3H, s), 5.70—6.00 (2H, m), 6.24 (1H, d-d, J=3 Hz, and 2 Hz), 7.20—7.60 (3H, m), 8.00—8.25 (2H, m). *Anal.* Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.61; H, 5.39; N, 6.90.

2,5-Dibenzoyloxy-1-methylpyrrole **10a**: Colorless needles from benzene–hexane, mp 117—118°. UV λ_{max}^{EtOH} nm (log ε): 234 (4.00), 269 (3.86), 277 (3.87), 295 (2.80). IR ν_{max}^{Nujol} cm^{-1}: 1740. Mass Spectrum *m/e*: 321 (M^+). NMR (CCl_4) δ: 3.35 (3H, s), 5.27 (2H, s). 7.30—7.80 (6H, m), 8.00—8.30 (4H, m). *Anal.* Calcd. for $C_{19}H_{15}O_4N$: C, 71.02; H, 4.71; N, 4.36. Found: C, 71.20; H, 4.72; N, 4.35.

Reaction of 1-Benzylpyrrole 8b with 1——A solution of **1** (484 mg, 2 mmoles) and **8b** (400 mg, 2.5 mmoles) in benzene (4 ml) was allowed to react (Table I) and the reaction mixture was worked up as above (TLC, benzene) to give **9b** (130 mg, 24%) and **10b** (140 mg, 35%).

2-Benzoyloxy-1-benzylpyrrole **9b**: Colorless needles from hexane, mp 44—45°. UV λ_{max}^{EtOH} nm (log ε): 231 (4.32), 276 (3.61), 283 (3.61), 300 (3.53). IR ν_{max}^{Nujol} cm^{-1}: 1755. Mass Spectrum *m/e*: 277 (M^+). NMR (CCl_4) δ: 4.94 (2H, s), 5.80—6.10 (2H, m), 6.23 (1H, m), 6.80—7.65 (8H, m), 7.75—8.10 (2H, m). *Anal.* Calcd. for $C_{18}H_{15}O_2N$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.96; H, 5.55; N, 5.06.

2,5-Dibenzoyloxy-1-benzylpyrrole **10b**: Colorless needles from benzene–hexane, mp 123—124°. UV λ_{max}^{EtOH} nm (log ε): 233 (4.55), 284 (3.86), 305 (3.81). IR ν_{max}^{Nujol} cm^{-1}: 1750. Mass Spectrum *m/e*: 397 (M^+). NMR (CCl_4) δ: 4.92 (2H, s), 3.90 (2H, s), 7.00—7.70 (11H, m), 7.75—8.05 (4H, m). *Anal.* calcd. for $C_{25}H_{19}O_4N$: C, 75.55; H, 4.82; N, 3.52. Found: C, 75.78; H, 4.90; N, 3.52.

Reaction of 1-Phenylpyrrole 8c with 1——A solution of **1** (1.21 g, 5 mmoles) and **8c** (858 mg, 6 mmoles) in acetonitrile (10 ml) was allowed to react (Table I) and evaporated *in vacuo*. The residue was dissolved in EtOAc, and the solution was worked up as in the case of **8a** (TLC, benzene–hexane=1: 2) to give **9c** (240 mg, 18%) and **10c** (100 mg, 10%).

2-Benzoyloxy-1-phenylpyrrole **9c**: bp 195—200°/3 mmHg. IR ν_{max}^{Film} cm^{-1}: 1750. Mass Spectrum *m/e*: 263 (M^+). NMR (CCl_4) δ: 6.05—6.30 (2H, m), 6.55—6.65 (1H, m), 7.10—7.60 (8H, m). 7.88—8.10 (2H, m). *Anal.* Calcd. for $C_{17}H_{13}O_2N$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.65; H, 4.92; N, 5.54.

2,5-Dibenzoyloxy-1-phenylpyrrole **10c**: Colorless needles from hexane, mp 87—88.5°. UV λ_{max}^{EtOH} nm (log ε): 232 (4.57), 276 (3.82), 284 (3.82). IR ν_{max}^{Nujol} cm^{-1}: 1745, 1760. Mass Spectrum *m/e*: 383 (M^+). NMR ($CDCl_3$) δ: 6.10 (2H, s), 7.00—7.70 (11H, m), 7.75—8.20 (4H, m). *Anal.* Calcd. for $C_{24}H_{17}O_4N$: C, 75.18; H, 4.47; N, 3.65. Found: C, 74.95; H, 4.36; N, 3.59.

Reaction of 1-*p*-Methoxyphenylpyrrole 8d with 1——A solution of **1** (242 mg, 1 mmole) and **8d**[30] (173 mg, 1 mmole) in benzene (6 ml) was allowed to react and worked up as above to give **9d** (80 mg, 28%) and **10d** (15 mg, 8%).

2-Benzoyloxy-*p*-methoxyphenylpyrrole **9d**: bp 215°/2 mmHg. IR ν_{max}^{Film} cm^{-1}: 1755. Mass Spectrum *m/e*: 293 (M^+). NMR ($CDCl_3$) δ: 3.66 (3H, s), 6.00—6.20 (2H, m), 6.50 (1H, m), 6.74 (2H, d, J=10 Hz). 7.20—7.50 (3H, m), 7.80—8.10 (2H, m), 7.20 (2H, d, J=10 Hz). *Anal.* Calcd. for $C_{18}H_{15}O_3N$: C, 73.70, H, 5.15; N, 4.78. Found: C, 73.78; H, 5.22; N, 4.73.

2,5-Dibenzoyloxy-1-*p*-methoxyphenylpyrrole **10d**: Colorless prisms from benzene–hexane, mp 137—138°. UV λ_{max}^{EtOH} nm (log ε): 232 (4.83), 276 (4.14). IR ν_{max}^{Nujol} cm^{-1}: 1755. Mass Spectrum *m/e*: 413 (M^+). NMR ($CDCl_3$) δ: 3.71 (3H, s), 6.06 (2H, s), 6.83 (2H, d, J=8 Hz), 7.10—7.70 (8H, m). 7.80—8.10 (4H, m). *Anal.* Calcd. for $C_{25}H_{19}O_5N$: C, 72.63; H, 4.63; N, 3.39. Found: C, 72.81; H, 4.70; N, 3.38.

2-(1-Methylpyrrolyl)phenylmethanol 18b——2-Benzoyl-1-methylpyrrole[31] was reduced with $LiAlH_4$ in ether as usual to give **18b** (32%); Slightly yellow viscous oil, bp 165—170°/3 mmHg. *Anal.* Calcd. for $C_{12}H_{13}ON$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.94; H, 6.87; N, 7.62.

Diphenyl-2-(1-methylpyrrolyl)methanol 18c——To a Grignard reagent prepared from Mg (310 mg, 13 matoms) and bromobenzene (2 g, 13 mmoles) in ether (10 ml) was added a solution of 2-benzoyl-1-methylpyrrole (1.85 g) in ether (10 ml) dropwise. The whole mixture was refluxed with stirring for 1.5 hr. After cooling small amount of ice was added and the mixture was dried (Na_2SO_4), filtered and evaporated to leave

29) Melting points are uncorrected. NMR spectra were recorded on Hitachi R-20B and R-24 spectrometers with TMS as internal standard. IR spectra were measured on a JASCO IR-S spectrophotometer, UV spectra on a Shimazu UV-200 spectrophotometer, and mass spectra on a Hitachi RMU-6E mass spectrometer. Thin-layer chromatography (TLC) was performed using Silica gel (Merck GF 254).

30) H. Goss and U. Beier, *Chem. Ber.*, **95**, 2270 (1962).

31) D.A. Shirley, B.H. Bross, and P.A. Roussel, *J. Org. Chem.*, **20**, 225 (1955).

18c (1.75 g, 50%): viscous oil. bp 176—180°/3 mmHg. IR ν_{max}^{Film} cm^{-1}: 3520. *Anal.* Calcd. for $C_{18}H_{17}ON$: C, 82.10; H, 6.51; N, 5.32. Found: C, 81.91; H, 6.48; N, 5.19.

N-Phenylpyrrole-2-methanol 18d——N-Phenyl-2-formylpyrrole[32] (3.1 g) was reduced with $LiAlH_4$ (800 mg) in ether (10 ml) as usual to give **18d** (2.7 g, 90%) as viscous oil: bp 125—132°/32 mmHg. *Anal.* Calcd. for $C_{11}H_{11}ON$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.06; H, 6.33; N, 8.00.

General Procedure for the Oxidation of Pyrrole-2-methanols 18 with 1 (Table II)——Equimolecular mixture of the methanol derivatives (1—3 mmoles) and **1** (1—3 mmoles) in benzene (3—6 ml) was stirred at room temperature. The reaction mixture was worked up as in the case of **8a**. **9** and/or **10** were obtained in the yields shown in Table II.

Formation of Benzaldehyde from the Oxidation of 18b with 1——The above reaction mixture of **18b** (2 mmoles) and **1** (2 mmoles) in benzene (6 ml) was extracted three times with 10% aq. $NaHSO_3$ (5 ml each). The combined aqueous layer was made weakly alkaline by adding $NaHCO_3$, extracted with ether. The ether layer was washed with H_2O, dried (Na_2SO_4) and evaporated to leave benzaldehyde (50 mg, 23%), which was identified as the 2,4-dinitrophenylhydrazone.

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