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Ring Transformation of 3,4-Diphenyl-2-furylcarbamoyl Compounds to N-Substituted 3,4-Diphenyl-5-hydroxy-3-pyrrolin-2-ones

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3,4-Diphenyl-2-furylcarbamoyls (IIIa—e) react with oxygen in benzene at room temperature and in the absence of catalysts or bases to give 3,4-diphenyl--5-hydroxy-3-pyrrolin-2-ones (Va—e) as main products. Under the same conditions, treatment of 3,4-diphenyl-2-furyl isocyanate (II) with an excess of various amines resulted in a clean autoxidation reaction to give Ve—h and diphenylmaleimides (XIIa—d) in a ratio of about 1: 1. 3-Hydroxyphenanthro[9,10-*c*]pyrrolin-1-ones (XIIIa—e) were prepared by the photocyclization of Va—e.

Keywords——autoxidation; 3,4-diphenyl-2-furylcarbamoyls; 3,4-diphenyl-5-hydroxy-3-pyrrolin-2-ones; ring transformation; ring-chain tautomerism; photolysis; 3-hydroxyphenanthro[9,10-*c*]pyrrolin-1-ones

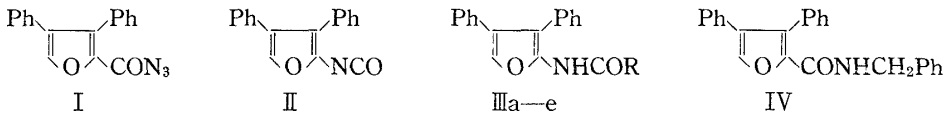
Recently we reported that the thermal cyclization of β-phenyl-α-furyl isocyanates gave furo[2,3-*c*]isoquinolin-5(4H)-ones in good yields.[2] In connection with this work, benzyl N-(3,4-diphenyl-2-furyl)carbamate (IIIa) was found to change to a higher melting point material upon recrystallization from benzene-petroleum benzin.[3] This observation led us study the autoxidation of 3,4-diphenyl-2-furylcarbamoyl compounds (IIIa—e).

We report here the novel ring transformation of 2-aminofuran derivatives (III) to 3,4-diphenyl-5-hydroxy-3-pyrrolinones (V) by mild autoxidation,[4] and a transformation of V to 3-hydroxyphenanthro[9,10-*c*]-pyrrolinones (XIII) by photocyclization.

A relative small group of organic substances, including certain electron-rich olefins,[5] hydrazines,[6] phenols[7] and enamines,[8] is known to react with oxygen at room temperature in the absence of catalysts or bases. Among them, 2-aminofurans[9] were only prepared recently by Coffen *et al.*[10] and Boyd *et al.*[11] They are rather unstable. In contrast, 2-furylcarbamoyls, which are 2-aminofuran derivatives, can be easily prepared by the reaction of various nucleophiles with 2-furyl isocyanates *via* the Curtius rearrangement of the corresponding azides.[12] Similarly, alkyl carbamates (IIIa—c) and benzyl thiocarbamate (IIId) were obtained from

1) Location: *Yagoto-Urayama, Tempaku-cho, Tempaku-ku, Nagoya 468, Japan.*
2) K. Ito, K. Yakushijin, S. Yoshina, A. Tanaka, and K. Yamamoto, *J. Heterocycl. Chem.*, **15**, 301 (1978); K. Yakushijin, *Yakugaku Zasshi*, **100**, 313 (1980).
3) Winters *et al.* reported that the thermal cyclization of β-phenyl-α-carbamoyl heterocyclic compounds produced fused isoquinolines: G. Winters and N.D. Mola, *Tetrahedron Lett.*, **1975**, 3877.
4) K. Ito and K. Yakushijin, *Heterocycles*, **9**, 1603 (1978).
5) R.W. Hoffmann, *Angew. Chem.*, **80**, 823 (1968).
6) S.F. Nelsen and R.T. Landis, *J. Am. Chem. Soc.*, **95**, 2719 (1973); E.G.E. Hawkina, *J. Chem. Soc.* (*C*), **1971**, 1474.
7) J. Carnduff and D.G. Leppard, *J.C.S. Perkin I*, **1976**, 2570; N.N. Gerber, *Can. J. Chem.*, **46**, 790 (1968).
8) J. Rigaudy, J. Barcelo, and C. Igier, *Bull. Soc. Chim. Fr.*, **1974**, 1151; E. Hoft, A.R. Katritzky, and M.R. Nesbit, *Tetrahedron Lett.*, **1967**, 3041; R.J. Sundberg, "The Chemistry of Indoles, Organic Chemistry, A series of Monographs," Vol. 18, Academic Press, New York, 1970, p. 282.
9) Simple aminofurans are rare; see, for example, A.P. Dunlop and F.N. Peters, "The Furans," Reinhold, New York, N.Y., 1953, p. 183.
10) J.F. Blount, D.L. Coffen, and D.A. Katonak, *J. Org. Chem.*, **43**, 3821 (1978).
11) G.V. Boyd and K. Heatherington, *J.C.S. Perkin I*, **1973**, 2523.
12) H.M. Singleton and W.R. Edwards, *J. Am. Chem. Soc.*, **60**, 540 (1938); H. Saikachi and K. Takai, *Yakugaku Zasshi*, **88**, 1189 (1968).

the reaction of 3,4-diphenyl-2-furoyl azide (I)[2] with appropriate alcohols and benzyl mercaptan as nucleophiles in boiling benzene. However, in the case of benzylamine as a nucleophile in the above treatment, the corresponding acid amide (IV) was obtained as a sole product instead of the desired carbamoylamine (IIIe). The carbamoylamine (IIIe) was only prepared by the thermal rearrangement of I to the isocyanate (II), followed by the addition of one equivalent of benzylamine.



a: R=OCH_2Ph, d: R=SCH_2Ph,
b: R=OCH_2CH_3, e: R=$NHCH_2Ph$
c: R=$OCH(CH_3)_2$,

Chart 1

Each furylcarbamoyl compound (III) was autoxidized by shaking with oxygen or air as an approximately 5% solution of benzene at one atm in daylight. In the case of IIIa, the deposition of colorless crystals was observed after several hours, and the reaction mixture was filtered after about 24 hr to give Va in 64% yield. The molecular formula of Va was found to be $C_{24}H_{19}NO_4$ on the basis of its elemental analysis data and molecular weight. The infrared (IR) spectrum of Va showed characteristic peaks at 3440, 1732 and 1688 cm^{-1} attributable to hydroxyl and carbonyl groups, respectively. The nuclear magnetic resonance (NMR) spectrum of Va showed a characteristic one proton doublet at δ 6.31 (d, J=4 Hz) coupled with a hydroxyl proton at δ 4.15 (d, J=4 Hz). Treatment of Va with acetic anhydride in pyridine at room temperature gave the acetate (Xa), and hydrogenolysis of Va with hydrogen over Pd/C in ethanol gave 3,4-diphenyl-3-pyrrolin-2-one (XI).[13] On the basis of these data, the structure of Va was assigned as N-carbobenzyloxy-3,4-diphenyl-5-hydroxy-3-pyrrolin-2-one. Furthermore, in this autoxidation of IIIa, diphenylacetylene (VI), diphenylmaleic anhydride (VII), 9,10-phenanthrenedicarboxylic anhydride (VIII) and N-carbobenzyloxyphenanthrene-9,10-carboximide (IXa) were obtained as by-products. The structures of VI, VII, and VIII were confirmed by direct comparison with samples prepared by the general route.[14,15] Compound IXa was identical with the compound prepared from Va by photocyclization as described below. The autoxidation is equally applicable to compounds (IIIb—e) to give the corresponding 5-hydroxypyrrolinones (Vb—e) as main products and VI, VII, VIII and IXb as by-products.

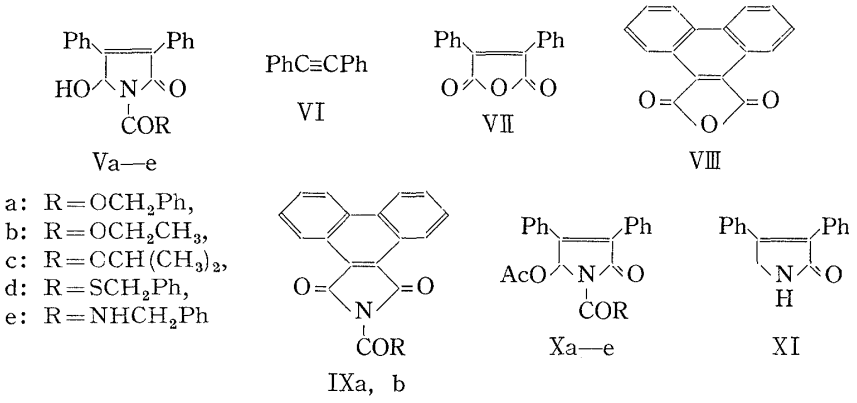


Chart 2

13) G. Rio and B. Serkiz, *Bull. Soc. Chim. Fr.*, **1976**, 1491.
14) C.L. Reimer, *Chem. Ber.*, **13**, 741 (1880).
15) A. Jeanes and R. Adams, *J. Am. Chem. Soc.*, **59**, 2608 (1937).

These autoxidations also proceeded in methanol instead of benzene as the solvent at room temperature. However, on reflux in these solvents, the starting materials was completely recovered.

On the other hand, treatment of the isocyanate (II) with an excess of various amines in benzene for 24 hr at room temperature resulted in clean autoxidation to give the corresponding 5-hydroxypyrrolinones (Ve—h) and diphenylmaleimides (XIIa—d) in a ratio of about 1: 1. In these cases, phenanethrene-type products were not observed. This seems to be due to the inhibition of radical formation on the reactant in the presence of amines. Compound XIIa was also derived from IIIa by autoxidation in benzene containing benzylamine.

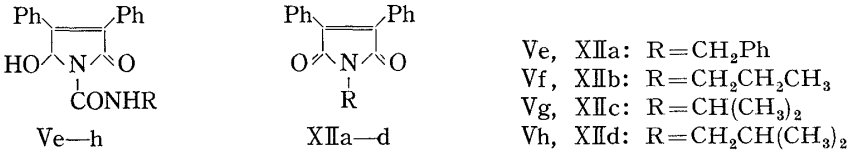


Chart 3

The mechanism involved in these autoxidations can be pictured as shown in Chart 4. The 1,4-cycloaddition of singlet oxygen with a five-membered diene system is well known. Thus, we postulated that the transient endoperoxide (XVII) was initially formed by the reaction of molecular oxygen with the electron-rich 2-aminofuran (III). The cleavage of XVII with loss of oxygen yields the γ-ketoamide (XVIII), which is spontaneously cyclized to 5-hydroxypyrrolinones (V) by ring-chain tautomerism. Another route requires opening with elimination of the amino group of XVII to yield maleic anhydride (VII). This pathway is preferable in the presence of bases, and VII is converted to maleimide (IX) and (XII) by treatment with amines.[16] Although the mechanism of the conversion of XVII to acetylene (VI) is not obvious, it may proceed *via* the formation of the cyclobutenedione (XIX) as described by Obata *et al.*[17]

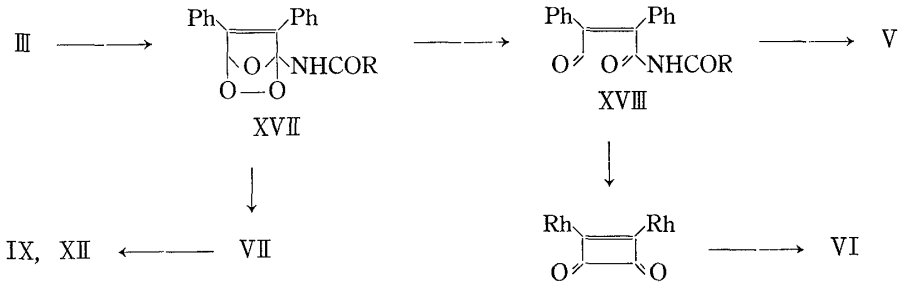


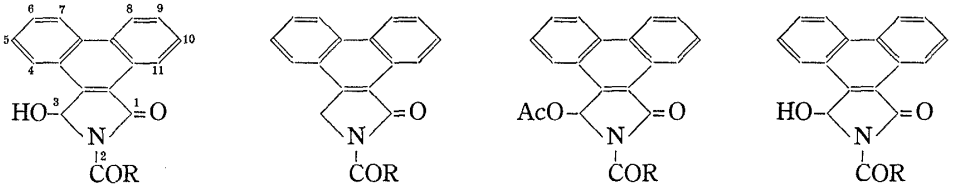
Chart 4

Finally, in connection with the above-mentioned studies of autoxidation, we examined the photolysis of Va in benzene to give colorless crystals, mp 185—186° in 70% yield. This reaction product corresponded to $C_{24}H_{17}NO_4$ and the NMR spectrum showed the presence of thirteen aromatic protons, of which four appeared at lower field [δ 8.26 (C-4), 8.83 (C-7, 8) and 9.05 (C-11)] as mutiplets. The IR spectrum showed absorption bands at 3382, 1770, 1740, 1681 cm^{-1} and the ultraviolet (UV) spectrum gave characteristic absorption bands at 212, 239, 251, 263, 281 and 315 nm, due to the phenanthrene nucleus. These spectral data suggested the formation of a new diaryl bond, and the structure of this reaction product was considered to be N-carbobenzyloxy-3-hydroxyphenanthro[9,10-*c*]pyrrolin-1-one (XIIIa).

16) U. Zehavi, *J. Org. Chem.*, **42**, 2819 (1977).
17) N. Obata and T. Takizawa, *Bull. Chem. Soc. Jpn.*, **50**, 2017 (1977).

Treatment of XIIIa with acetic anhydride in pyridine at room temperature gave the acetate (XVa), and hydrogenolysis of XIIIa with hydrogen over Pd/C in ethanol gave 3-hydroxyphenanthro[9, 10-*c*]pyrrolin-1-one (XVI). Furthermore, in this photolysis of Va, IXa and its dehydroxy compound XIV were obtained as by-products. Similarly, the photolysis of Vb—e gave the corresponding phenanthro[9,10-*c*]pyrrolinones (XIIIb—e) as main products.

Applications of these novel ring transformations to the synthesis of natural products are now being investigated.



XIIIa—e XIV XVa—e XVI

a: R=OCH_2Ph, d: R=SCH_2Ph,
b: R=OCH_2CH_3, e: R=$NHCH_2Ph$
c: R=$OCH(CH_3)_2$,

Chart 5

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Proton NMR spectra were recorded using a JEOL PS-100 spectrometer with tetramethylsilane as an internal standard. The IR spectra were taken on a Jasco IR-A-1 spectrometer. Mass spectra (MS) were obtained with a Hitachi RMU-6 spectrometer operating at an ionization potential of 70 eV. Irradiation was carried out with a 100 W high pressure mercury lamp, Taika HLV-B.

Benzyl N-(3,4-Diphenyl-2-furyl)carbamate (IIIa)——A solution of 3,4-diphenyl-2-furoyl azide (I)[2] (1 g, 3.5 mmol) and benzyl alcohol (1.5 g, 13.9 mmol) in benzene (15 ml) was stirred under reflux for 2 hr. Removal of the benzene by evaporation gave colorless crystals and recrystallization from ether afforded IIIa as colorless needles (1.2 g, 94%), mp 107—108°. IR ν_{max}^{KBr} cm^{-1}: 3350, 1720. MS *m/e*: 369 (M^+), 325, 261, 234, 206, 179. NMR ($CDCl_3$) δ: 5.16 (2H, s, CH_2), 6.43 (1H, br s, NH), 7.28 (15H, m, arom.-H), 7.43 (1H, s, C-5). *Anal.* Calcd for $C_{24}H_{19}NO_3$: C, 78.03; H, 5.18; N, 3.79. Found: C, 78.31; H, 5.17; N, 3.68.

Ethyl N-(3,4-Diphenyl-2-furyl)carbamate (IIIb)——The procedure described above was employed. IIIb: colorless syrups (97%). IR ν_{max}^{KBr} cm^{-1}: 3260, 1710. NMR ($CDCl_3$) δ: 1.21, 4.15 (5H, C_2H_5), 6.38 (1H, br s, NH), 7.26 (10H, m, arom.-H), 7.38 (1H, s, C-5). *Anal.* Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.52; H, 5.80; N, 4.76.

Isopropyl N-(3,4-Diphenyl-2-furyl)carbamate (IIIc)——The procedure described above was employed. IIIc: colorless needles (95%), mp 123—124°. IR $\nu_{max}^{KBr}$$cm^{-1}$: 3260, 1700. NMR ($CDCl_3$) δ: 1.19, 1.25, 4.93 (7H, isopro.-H), 6.32 (1H, br s, NH), 7.20 (10H, m, arom.-H), 7.36 (1H, s, C-5). *Anal.* Calcd for $C_{20}H_{19}NO_3$: C, 74.74; H, 5.96; N, 4.36. Found: C, 74.81; H, 6.11; N, 4.40.

Benzyl N-(3,4-Diphenyl-2-furyl)thiocarbamate (IIId)——The procedure described above was employed. IIId: colorless needles (85%), mp 137—138°. IR ν_{max}^{KBr} cm^{-1}: 3150, 1650. NMR ($CDCl_3$) δ: 4.11 (2H, s, CH_2), 7.24 (16H, m, NH and arom.-H), 7.40 (1H, s, C-5). *Anal.* Calcd for $C_{24}H_{19}NO_2S$: C, 74.78; H, 4.97; N, 3.63. Found: C, 74.89; H, 5.05; N, 3.77.

Benzyl N-(3,4-Diphenyl-2-furyl)carbamoylamine (IIIe)——A solution of I (1 g, 3.5 mmol) in benzene (15 ml) was stirred under reflux for 2 hr. After cooling, benzylamine (0.38 g, 3.5 mmol) was added to the above solution, and the reaction was continued for 0.5 hr at room temperature. Removal of the benzene gave IIIe as colorless needles (1 g, 78%), mp 165—166°. IR ν_{max}^{KBr} cm^{-1}: 3300, 1643. NMR ($CDCl_3$) δ: 4.34 (2H, d, J=6 Hz, CH_2, collapsing to a singlet with D_2O), 5.40 (1H, t, J=6 Hz, NH, vanishing with D_2O), 6.65 (1H, br s, NH, vanishing with D_2O), 7.18 (15H, m, arom.-H), 7.32 (1H, s, C-5). *Anal.* Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.29; H, 5.52; N, 7.69.

N-Benzyl-N-(3,4-diphenyl-2-furyl)carboxamide (IV)——The procedure described for IIIa was employed. IV: colorless needles (85%), mp 149—150°. IR ν_{max}^{KBr} cm^{-1}: 3400, 1655. NMR ($CDCl_3$) δ: 4.50 (2H, d, J=6 Hz, CH_2), 6.38 (1H, t, J=6 Hz, NH), 7.31 (15H, m, arom.-H), 7.59 (1H, s, C-5). *Anal.* Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 82.05; H, 5.45; N, 3.99.

Autoxidation of IIIa——A solution of IIIa (1 g, 2.7 mmol) in benzene (20 ml) was stirred under oxygen at 1 atm in daylight. After 24 hr, 55 ml of oxygen had been absorbed (theory, 60 ml) and uptake ceased. After concentration, the reaction mixture was filtered and the residue was recrystallized from chloroform to

give N-carbobenzyloxy-3,4-diphenyl-5-hydroxy-3-pyrrolin-2-one (Va) as colorless needles (670 mg, 64%), mp 170—171°. IR ν_{max}^{KBr} cm^{-1}: 3440, 1732, 1688. MS *m/e*: 385 (M$^+$), 340, 279, 261, 251, 179. NMR ($CDCl_3$) δ: 4.15 (1H, d, J=4 Hz, OH, vanishing with D_2O), 5.31 (2H, s, CH_2), 6.31 (1H, d, J=4 Hz, C-5, collapsing to a singlet with D_2O), 7.24 (15H, br s, arom.-H). *Anal.* Calcd for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.97; N, 3.63. Found: C, 74.99; H, 5.25; N, 3.88.

The mother liquor was concentrated and the residue was chromatographed on silica gel. Diphenylacetylene (VI, 8.7 mg, 2%) was obtained from the eluate with hexane. Elution with benzene gave diphenylmaleic anhydride (VII, 28 mg, 4%), mp 153—155° (lit.,[14] mp 155—156°) and 9,10-phenanthrenedicarboxylic anhydride (VIII, 5 mg, 4%), mp 316—318° (lit.,[15] mp 321—322°). Further elution with benzene gave a small amount of N-carbobenzyloxyphenanthrene-9,10-dicarboximide (IXa) as pale yellow needles (16 mg, 2%), mp 229—230°. IR ν_{max}^{KBr} cm^{-1}: 1774, 1735, 1700. MS *m/e*: 381 (M$^+$), 337, 247, 204, 190, 176. NMR ($CDCl_3$) δ: 5.49 (2H, s, CH_2), 7.39, 7.80 (9H, m, arom.-H), 8.71 (2H, m, C-7,8), 9.13 (2H, m, C-4,11). *Anal.* Calcd for $C_{24}H_{15}NO_4$: C, 75.58; H, 3.96; N, 3.67. Found: C, 75.60, H, 4.21; N, 3.80.

Autoxidation of IIIb——A solution of IIIb (0.5 g, 1.6 mmol) in benzene (10 ml) was stirred under oxygen in the manner described above. After 24 hr, uptake ceased. After concentration, the reaction mixture was filtered and the residue was recrystallized from ethanol to give N-carbethoxy-3,4-diphenyl-5-hydroxy-3-pyrrolin-2-one (Vb) as colorless needles (326 mg, 62%), mp 201—202°. IR ν_{max}^{KBr} cm^{-1}: 3438, 1720, 1689. MS *m/e*: 323 (M$^+$), 277, 251, 249, 222, 207, 179. NMR ($CDCl_3$) δ: 1.39, 4.33 (5H, C_2H_5), 4.30 (1H, d, J= 5 Hz, OH, vanishing with D_2O), 6.30 (1H, d, J=5 Hz, C-5, collapsing to a singlet with D_2O), 7.22 (10H, m, arom.-H). *Anal.* Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.30; H, 4.33. Found: C, 70.35; H, 5.32; N, 4.06.

The mother liquor was concentrated and the residue was chromatographed on silica gel. Small amounts of VI, VII and VIII were obtained from the eluate with hexane and benzene. Further elution with benzene gave N-carbethoxyphenanthrene-9,10-dicarboximide (IXb) as pale yellow needles (10 mg, 2%), mp 237—240°. IR ν_{max}^{KBr} cm^{-1}: 1780, 1745, 1708. MS *m/e*: 319 (M$^+$), 274, 260, 247, 236, 203, 190, 179, 176. NMR ($CDCl_3$) δ: 1.49, 4.47 (5H, C_2H_5), 7.74 (4H, m, arom.-H), 8.62 (2H, m, C-7,8), 9.05 (2H, m, C-4,11). *Anal.* Calcd for $C_{19}H_{13}NO_4$: C, 71.47; H, 4.10; N, 4.39. Found: C, 71.32; H, 4.05; N, 4.20.

Autoxidation of IIIc——A solution of IIIc (0.5 g, 1.6 mmol) in benzene (10 ml) was stirred under oxygen as described above. After 4 days, uptake ceased. Thin-layer chromatography (TLC) of the reaction mixture indicated the presence of many products. After concentration, the residue was chromatographed on silica gel. Elution with chloroform gave N-carboisopropyloxy-3,4-diphenyl-5-hydroxy-3-pyrrolin-2-one (Vc) as colorless needles (226 mg, 43%), mp 159—160°. IR ν_{max}^{KBr} cm^{-1}: 3440, 1737, 1680. NMR ($CDCl_3$) δ: 1.37, 1.44, 5.19 (7H, isopro.-H), 4.51 (1H, d, J=5 Hz, OH, vanishing with D_2O), 6.43 (1H, d, J=5 Hz, C-5, collapsing to a singlet with D_2O), 7.36 (10H, br s, arom.-H). *Anal.* Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.16; H, 5.69; N, 4.06.

Autoxidation of IIId——(a) A solution of IIId (0.5 g, 1.3 mmol) in benzene (10 ml) was stirred under oxygen as described above. TLC of the reaction mixture indicated the presence of many products. After concentration, the residue was chromatographed on silica gel. Elution with chloroform gave N-carbothiobenzyloxy-3,4-diphenyl-5-hydroxy-3-pyrrolin-2-one (Vd) as colorless needles (110 mg, 21%), mp 169—170°. IR ν_{max}^{KBr} cm^{-1}: 3440, 1713, 1618. MS *m/e*: 401 (M$^+$), 251, 237, 207, 180, 178. NMR ($CDCl_3$) δ: 4.22 (2H, s, CH_2), 4.41 (1H, br d, J=4 Hz, OH, vanishing with D_2O), 6.51 (1H, br d, J=4 Hz, C-5, collapsing to a singlet with D_2O), 7.34 (15H, br s, arom.-H). *Anal.* Calcd for $C_{24}H_{19}NO_3S$: C, 71.80; H, 4.77; N, 3.49. Found: C, 71.67; H, 4.59; N, 3.33.

(b) A solution of IIId (0.5 g, 1.3 mmol) was stirred under air at 1 atm in daylight for 24 hr. After concentration, the resulting crystals were filtered off and recrystallized from methanol to give Vd (70 mg, 13%). The mother liquor was left to stand for 8 months at room temperature. This reaction mixture was chromatographed on silica gel. Small amounts of VII and VIII were obtained from the eluate with benzene. Further elution with chloroform gave Vd (25 mg, 5%) and N-carbothiobenzyloxy-3-hydroxyphenanthro-[9,10-*c*]pyrrolin-1-one (XIIId) as colorless needles (250 mg, 48%), mp 248—250°. IR ν_{max}^{KBr} cm^{-1}: 3410, 1718, 1625. MS *m/e*: 399 (M$^+$), 291, 247, 233, 204, 177, 176. NMR (DMSO-d_6) δ: 4.30 (2H, s, CH_2), 6.84 (1H, d, J=9 Hz, C-3, collapsing to a singlet with D_2O), 7.40 (5H, m, arom.-H), 7.48 (1H, d, J=9 Hz, OH, vanishing with D_2O), 8.29 (1H, m, C-4), 8.96 (3H, m, C-7, 8, 11). *Anal.* Calcd for $C_{24}H_{17}NO_3S$: C, 72.16; H, 4.29; N, 3.51. Found: C, 72.05; H, 4.12; N, 3.37.

Autoxidation of IIIe——A suspension of IIIe (0.5 g, 1.4 mmol) in benzene (30 ml) was stirred under oxygen in daylight for 24 hr. TLC of the reaction mixture indicated the presence of many products. After concentration, the resulting crystals were filtered off and recrystallized from methanol to give N-carbobenzylamino-3,4-diphenyl-5-hydroxy-3-pyrrolin-2-one (Ve) as colorless needles (200 mg, 38%), mp 164—166°. IR ν_{max}^{KBr} cm^{-1}: 3340, 1688, 1662. MS *m/e*: 384 (M$^+$), 366, 323, 261, 251, 235, 206, 179, 178. NMR ($CDCl_3$) δ: 4.54 (2H, d, J=6 Hz, CH_2), 4.90 (1H, d, J=4 Hz, OH, vanishing with D_2O), 6.49 (1H, d, J=4 Hz, C-5, collapsing to a singlet with D_2O), 7.28 (15H, br s, arom.-H), 8.55 (1H, t, J=6 Hz, NH). *Anal.* Calcd for $C_{24}H_{26}N_2O_3$: C, 74.98; H, 5.24; N, 7.29. Found: C, 75.02; H, 5.39; N, 7.38.

Acetylation of Va—e——Acetylation of Va—e (100 mg) with acetic anhydride (0.5 ml) and pyridine (1.5 ml) at room temperature for 5 hr, followed by the usual work-up and recrystallization from ether gave N-substituted 5-acetoxy-3,4-diphenyl-3-pyrrolin-2-ones (Xa—e) quantitatively. The physical properties

are given below.

N-Carbobenzyloxy-5-acetoxy-3,4-diphenyl-3-pyrrolin-2-one (Xa): Colorless needles, mp 168—169°. IR ν_{max}^{KBr} cm^{-1}: 1783, 1755, 1738, 1724. NMR ($CDCl_3$) δ: 1.80 (3H, s, CH_3), 5.18, 5.43 (2H, d×2, J=12 Hz, CH_2), 7.29 (15H, m, arom.-H), 7.72 (1H, s, C-5). *Anal.* Calcd for $C_{26}H_{21}NO_5$: C, 73.05; H, 4.95; N, 3.28. Found: C, 72.89; H, 4.80; N, 3.18.

N-Carbethoxy-5-acetoxy-3,4-diphenyl-3-pyrrolin-2-one (Xb): Colorless needles, mp 130—131°. IR ν_{max}^{KBr} cm^{-1}: 1775, 1757, 1735, 1712. NMR ($CDCl_3$) δ: 1.39, 4.43 (5H, C_2H_5), 1.99 (3H, s, CH_3), 7.33 (10H, br s, arom.-H), 7.76 (1H, s, C-5). *Anal.* Calcd for $C_{21}H_{19}NO_5$: C, 69.03; N, 5.24; N, 3.83. Found: C, 69.00; H, 5.20; N, 3.81.

N-Carboisopropyloxy-5-acetoxy-3,4-diphenyl-3-pyrrolin-2-one (Xc): Colorless needles, mp 135—136°. IR ν_{max}^{KBr} cm^{-1}: 1784, 1773, 1765, 1750. NMR ($CDCl_3$) δ: 1.35, 1.39, 5.20 (7H, isopro.-H), 1.97 (3H, s, CH_3), 7.32 (10H, m, arom.-H), 7.74 (1H, s, C-5). *Anal.* Calcd for $C_{22}H_{21}NO_5$: C, 69.64; H, 5.58; N, 3.69. Found: C, 69.52; H, 5.49; N, 3.58.

N-Carbothiobenzyloxy-5-acetoxy-3,4-diphenyl-3-pyrrolin-2-one (Xd): Colorless needles, mp 141—142°. IR ν_{max}^{KBr} cm^{-1}: 1748, 1702, 1638. NMR ($CDCl_3$) δ: 1.92 (3H, s, CH_3), 4.14 (2H, s, CH_2), 7.22 (15H, m, arom.-H), 7.72 (1H, s, C-5). *Anal.* Calcd for $C_{26}H_{21}NO_4S$: C, 70.48; H, 4.77; N, 3.16. Found: C, 70.25; H, 4.65; N, 3.12.

N-Carbobenzylamino-5-acetoxy-3,4-diphenyl-3-pyrrolin-2-one (Xe): Colorless needles, mp 152—153°. IR ν_{max}^{KBr} cm^{-1}: 3285, 1798, 1732, 1638. NMR ($CDCl_3$) δ: 1.97 (3H, s, CH_3), 4.51 (2H, d×2, J=5.7 Hz, CH_2), 7.29 (15H, m, arom.-H), 7.82 (1H, s, C-5), 8.45 (1H, br t, J=5.7 Hz, NH). *Anal.* Calcd for $C_{26}H_{22}N_2O_4$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.21; H, 5.15; N, 6.49.

3,5-Diphenyl-3-pyrrolin-2-one (XI)——A mixture of Va (0.2 g, 0.5 mmol) in ethanol (10 ml) containing 5% Pd/C (50 mg) was hydrogenated at room temperature. The reaction mixture was filtered and the solvent was evaporated off to give XIa as colorless needles, (99 mg, 77%), mp 192—193° (lit.,[13] mp 194—195°). IR ν_{max}^{KBr} cm^{-1}: 3170, 3040, 1670. MS *m/e*: 235 (M^+), 206, 191, 178. NMR ($CDCl_3$) δ: 4.44 (2H, d, J=1 Hz, C-5), 7.40 (11H, m, NH and arom.-H). *Anal.* Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.66; H, 5.50; N, 5.79.

Reaction of 3,4-Diphenyl-2-furyl Isocyanate (II) with Excess Benzylamine——A solution of I (0.5 g, 1.7 mmol) in benzene (10 ml) was stirred under reflux for 2 hr. After cooling, benzylamine (0.4 g, 3.7 mmol) was added, and the reaction was continued for 24 hr. The reaction mixture was washed with water and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene gave N-benzyl diphenylmaleimide (XIIa) as yellow needles (188 mg, 32%, fluorescence), mp 127—128°. IR ν_{max}^{KBr} cm^{-1}: 1745, 1683, 1590. NMR ($CDCl_3$) δ: 4.79 (2H, s, CH_2), 7.29 (15H, m, arom.-H). *Anal.* Calcd for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13. Found: C, 81.29; H, 5.00; N, 4.12.

Further elution with chloroform gave Ve (190 mg, 29%).

Reaction of II with Excess Propylamine——The procedure described above was employed. N-Propyl diphenylmaleimide (XIIb) and N-carbopropylamino-5-hydroxy-3,4-diphenyl-3-pyrrolin-2-one (Vf) were obtained. XIIb; yellow needles (175 mg, 35%, fluorescence), mp 92—93°. IR ν_{max}^{KBr} cm^{-1}: 1752, 1683, 1592. NMR ($CDCl_3$) δ: 0.96, 1.70, 3.57 (7H, propyl-H), 7.34 (10H, m, arom.-H). *Anal.* Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.45; H, 5.82; N, 4.82. Vf; colorless needles (190 mg, 33%), mp 126—127°. IR ν_{max}^{KBr} cm^{-1}: 3400, 3300, 1695, 1670. NMR ($CDCl_3$) δ: 0.98, 1.61, 3.31 (7H, propyl-H), 4.90 (1H, br, OH), 6.51 (1H, s, C-5), 7.34 (10H, br s, arom.-H), 8.20 (1H, br t, NH). *Anal.* Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 70.86; H, 5.93; N, 8.14.

Reaction of II with Excess Isopropylamine——The procedure described above was employed. N-Isopropyl diphenylmaleimide (XIIc) and N-carboisopropylamino-5-hydroxy-3,4-diphenyl-3-pyrrolin-2-one (Vg) were obtained. XIIc; yellow needles (160 mg, 30%, fluorescence), mp 135—136°. IR ν_{max}^{KBr} cm^{-1}: 1752, 1688, 1593. NMR ($CDCl_3$) δ: 1.44, 1.52, 4.45 (7H, isopro.-H), 7.33 (10H, m, arom.-H). *Anal.* Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.21; H, 5.72; N, 4.69. Vg; colorless needles (170 mg, 29%), mp 162—163°. IR ν_{max}^{KBr} cm^{-1}: 3400, 3280, 1692, 1665. NMR ($CDCl_3$) δ: 1.23, 1.29, 4.09 (7H, isopro.-H), 4.90 (1H, d, J=4 Hz, OH), 6.50 (1H, d, J=4 Hz, C-5), 7.31 (10H, m, arom.-H), 8.07 (1H, br d, NH). *Anal.* Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.32; H, 5.88; N, 8.29.

Reaction of II with Excess Isobutylamine——The procedure described above was employed. N-Isobutyl diphenylmaleimide (XIId) and N-carboisobutylamino-5-hydroxy-3,4-diphenyl-3-pyrrolin-2-one (Vh) were obtained. XIId; yellow needles (180 mg, 34%, fluorescence), mp 101—102°. IR ν_{max}^{KBr} cm^{-1}: 1754, 1688, 1594. NMR ($CDCl_3$) δ: 0.93, 1.00, 2.10, 3.44 (9H, isobutyl-H), 7.31 (10H, m, arom.-H). *Anal.* Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.76; H, 6.25; N, 4.51. Vh; colorless needles (170 mg, 28%), mp 155—156°. IR ν_{max}^{KBr} cm^{-1}: 3340, 3290, 1694, 1668. NMR ($CDCl_3$) δ: 0.95, 1.01, 1.86, 3.19 (9H, isobutyl-H), 4.92 (1H, br, OH), 6.51 (1H, s, C-5), 7.31 (10H, m, arom.-H), 8.26 (1H, br t, NH). *Anal.* Calcd for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 8.00. Found: C, 71.74; H, 6.27; N, 7.93.

Photolysis of Va——A solution of Va (0.5 g, 1.3 mmol) in benzene (400 ml) was irradiated for 3 hr. After removal of the solvent, the residue was treated with ether and the resulting crystals were filtered off. Recrystallization from chloroform gave N-carbobenzylouy-3-hydroxyphenanthro[9,10-*c*]pyrrolin-1-one (XIIIa) as colorless needles (350 mg, 70%), mp 185—186°. IR ν_{max}^{KBr} cm^{-1}: 3382, 1770, 1740, 1681. NMR (DMSO-d_6)

δ: 5.40 (2H, s, CH_2), 6.68 (1H, d, J=9 Hz, C-3, collapsing to a singlet with D_2O), 7.25 (1H, d, J=9 Hz, OH, vanishing with D_2O), 7.44 (5H, m, arom.-H), 7.79 (4H, m, C-5, 6, 9, 10), 8.26 (1H, m, C-4), 8.83 (2H, m, C-7, 8), 9.05 (1H, m, C-11). *Anal.* Calcd for $C_{24}H_{17}NO_4$: C, 75.18; H, 4.47; N, 3.65. Found: C, 75.16; H, 4.42; N, 3.60.

Further concentration of the chloroform layer provided a residue, which was subjected to preparative TLC [silica gel, developed with $CHCl_3$] to give IXa (20 mg, 4%) and N-carbobenzyloxyphenanthro[9,10-*c*]-pyrrolin-1-one (XIV, 14 mg, 3%) as colorless needles, mp 196—197°. IR ν_{max}^{KBr} cm^{-1}: 1763, 1700. MS *m/e*: 367 (M^+), 323, 260, 233, 204, 177. NMR ($CDCl_3$) δ: 4.83 (2H, s, C-3), 5.40 (2H, s, CH_2), 7.52 (10H, m, arom.-H), 8.51 (2H, m, C-7, 8), 9.11 (1H, m, C-11). *Anal.* Calcd for $C_{24}H_{17}NO_3$: C, 78.46; H, 4.66; N, 3.81. Found: C, 78.39; H, 4.62; N, 3.75.

Photolysis of Vb——The procedure described above was employed. N-Carbethoxy-3-hydroxyphenanthro[9,10-*c*]pyrrolin-1-one (XIIIb) was obtained as colorless needles (63%), mp 232—233°. IR ν_{max}^{KBr} cm^{-1}: 3380, 1780, 1733, 1698. NMR (DMSO-d_6) δ: 1.42, 4.39 (5H, C_2H_5), 6.71 (1H, d, J=9 Hz, C-3, collapsing to a singlet with D_2O), 7.23 (1H, d, J=9 Hz, OH, vanishing with D_2O), 7.83 (4H, m, arom.-H), 8.30 (1H, m, C-4), 8.89 (2H, m, C-7, 8), 9.10 (1H, m, C-11). *Anal.* Calcd for $C_{19}H_{15}NO_4$: C, 71.02; H, 4.71; N, 4.36. Found: C, 71.00; H, 4.69; N, 4.25.

Photolysis of Vc——The procedure described above was employed. N-Carboisopropyloxy-3-hydroxyphenanthro[9,10-*c*]pyrrolin-1-one (XIIIc) was obtained as colorless needles (68%), mp 198—199°. IR ν_{max}^{KBr} cm^{-1}: 3360, 1730, 1702. NMR (DMSO-d_6) δ: 1.40, 1.46, 5.09 (7H, isopro.-H), 6.45 (1H, d, J=9 Hz, C-3, collapsing to a singlet with D_2O), 7.07 (1H, d, J=9 Hz, OH, vanishing with D_2O), 7.68 (4H, m, arom.-H), 8.11 (1H, m, C-4), 8.66 (2H, m, C-7, 8), 8.94 (1H, m, C-11). *Anal.* Calcd for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11; N, 4.18. Found: C, 71.56; H, 5.10; N, 4.12.

Photolysis of Vd——The procedure described above was employed. XIIId was obtained in 55% yield.

Photolysis of Ve——The procedure described above was employed. N-Carbobenzylamino-3-hydroxyphenanthro[9,10-*c*]pyrrolin-1-one (XIIIe) was obtained as colorless needles (69%), mp 262—263°. IR ν_{max}^{KBr} cm^{-1}: 3260, 1695, 1650. NMR (DMSO-d_6) δ: 4.58 (2H, d, J=6 Hz, CH_2), 6.74 (1H, d, J=8 Hz, C-3, collapsing to a singlet with D_2O), 7.19 (1H, d, J=8 Hz, OH, vanishing with D_2O), 7.35 (5H, m, arom.-H), 7.76 (4H, m, arom.-H), 8.25 (1H, m, C-4), 8.81 (4H, m, C-7, 8, 11 and NH). *Anal.* Calcd for $C_{24}H_{18}N_2O_3$: C, 75.38; H, 4.74; N, 7.33. Found: C, 75.26; H, 4.61; N, 7.25.

Acetylation of XIIIa—e——Acetylation of XIIIa—e (50 mg) with acetic anhydride (0.5 ml) and pyridine (1.5 ml) at room temperature for 5 hr followed by the usual work-up and recrystallization from chloroform gave N-substituted 5-acetoxyphenanthro[9,10-*c*]pyrrolin-1-ones (XVa—e) quantitatively.

N-Carbobenzyloxy-3-acetoxyphenanthro[9,10-*c*]pyrrolin-1-one (Va): Colorless needles, mp 183—184°. IR ν_{max}^{KBr} cm^{-1}: 1780, 1735. NMR (DMSO-d_6) δ: 2.00 (3H, s, CH_3), 5.26, 5.43 (2H, d×2, J=12 Hz, CH_2), 7.42 (5H, m, arom.-H), 7.74 (5H, m, arom.-H), 7.77 (1H, s, C-3), 8.81 (3H, m, C-7, 8, 11). *Anal.* Calcd for $C_{26}H_{19}NO_5$: C, 73.40; H, 4.50; N, 3.29. Found: C, 73.29; H, 4.32; N, 3.16.

N-Carbethoxy-3-acetoxyphenanthro[9,10-*c*]pyrrolin-1-one (Vb): Colorless prisms, mp 237—238°. IR ν_{max}^{KBr} cm^{-1}: 1770, 1732, 1695. NMR ($CDCl_3$) δ: 1.46, 4.39 (5H, C_2H_5), 2.13 (3H, s, CH_3), 7.60 (4H, m, arom.-H), 7.79 (1H, s, C-3), 7.84 (1H, m, C-4), 8.50 (2H, m, C-7, 8), 9.04 (1H, m, C-11). *Anal.* Calcd for $C_{21}H_{19}NO_5$: C, 69.41; H, 4.72; N, 3.86. Found: C, 69.36; H, 4.61; N, 3.75.

N-Carboisopropyloxy-3-acetoxyphenanthro[9,10-*c*]pyrrolin-1-one (XVc): Colorless prisms, mp 204—205°. IR ν_{max}^{KBr} cm^{-1}: 1763, 1740, 1692. NMR ($CDCl_3$) δ: 1.42, 1.46, 5.17 (7H, isopro.-H), 2.12 (3H, s, CH_3), 7.57 (4H, m, arom.-H), 7.68 (1H, s, C-3), 7.77 (1H, m, C-4), 8.41 (2H, m, C-7, 8), 8.98 (1H, m, C-11). *Anal.* Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71. Found: C, 69.90; H, 4.96; N, 3.66.

N-Carbothiobenzyloxy-3-acetoxyphenanthro[9,10-*c*]pyrrolin-1-one (XVd): Colorless prisms, mp 238—239. IR ν_{max}^{KBr} cm^{-1}: 1740, 1718, 1629. NMR ($CDCl_3$) δ: 2.12 (3H, s, CH_3), 4.31 (2H, s, CH_2), 7.34 (5H, m, arom.-H), 7.70 (4H, m, arom.-H), 7.88 (1H, s, C-3), 7.94 (1H, m, C-4), 8.60 (2H, m, C-7, 8), 9.04 (1H, m, C-11). *Anal.* Calcd for $C_{26}H_{19}NO_4S$: C, 70.75; H, 4.31; N, 3.17. Found: C, 70.55; H, 4.27; N, 2.96.

N-Carbobenzylamino-3-acetoxyphenanthro[9,10-*c*]pyrrolin-1-one (XVe): Colorless prisms, mp 199—200°. IR ν_{max}^{KBr} cm^{-1}: 3300, 1740, 1700, 1670. NMR ($CDCl_3$) δ: 2.12 (3H, s, CH_3), 4.58 (2H, d×2, J=5.5 Hz, CH_2), 7.34 (5H, m, arom.-H), 7.60 (4H, m, arom.-H), 7.75 (1H, s, C-3), 7.87 (1H, m, C-4), 8.51 (3H, m, C-7, 8 and NH), 8.87 (1H, m, C-11). *Anal.* Calcd for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.42; H, 4.65; N, 6.45.

3-Hydroxyphenanthro[9,10-*c*]pyrrolin-1-one (XVI)——A mixture of XIIIa (0.1 g, 0.26 mmol) in ethanol (10 ml) containing 5% Pd/C was hydrogenated at room temperature. The reaction mixture was filtered and the solvent was evaporated off to give XVI (60 mg, 92%) as colorless prisms, mp 292—294°. IR ν_{max}^{KBr} cm^{-1}: 3340, 3195, 1684. MS *m/e*: 249 (M^+), 233, 204, 176. NMR (DMSO-d_6) δ: 6.27 (1H, br s, C-3, collapsing to a siglet with D_2O), 6.50 (1H, br, OH, vanishing with D_2O), 7.72 (4H, m, arom.-H), 8.27 (1H, m, C-4), 8.81 (3H, m, C-7, 8 and NH), 9.12 (1H, m, C-11). *Anal.* Calcd for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.45; N, 5.62. Found: C, 77.00; H, 4.35; N, 5.46.