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EFFECT OF METAL IONS IN ORGANIC SYNTHESIS. PART XXXIII. 2-HYDROXY-4-PYRROLINES AS STABLE INTERMEDIATES IN THE SYNTHESIS OF 1-AMINOPYRROLE DERIVATIVES

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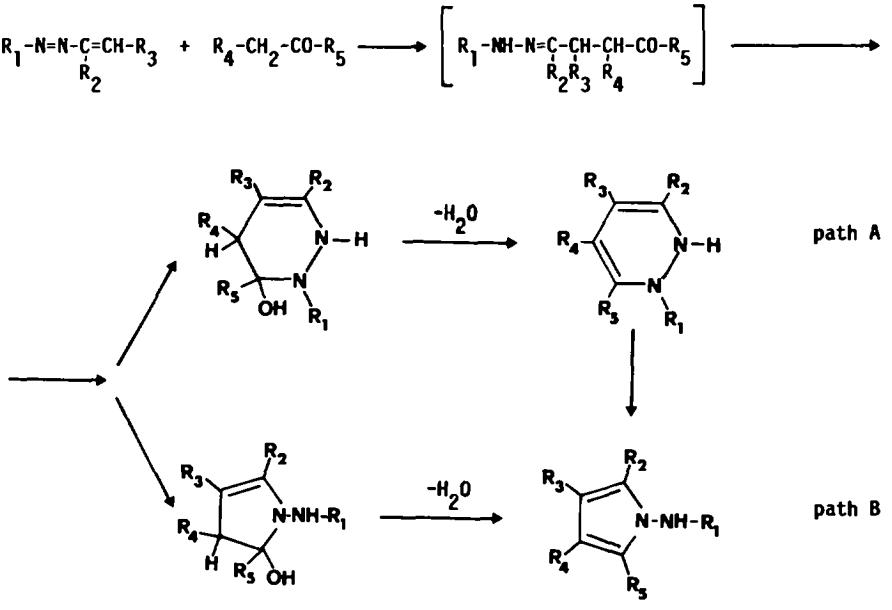
Abstract - The reactions of conjugated aroylazoalkenes with ß-diketones and ß-ketoesters in the presence and in the absence of copper(II) chloride as catalyst have been studied. In the first case, 1-aminopyrrole derivatives have been obtained, while in the second case the formation of 2-hydroxy-4-pyrrolines as stable intermediates has been frequently detected. The observations on the conditions of the formation of either or both products, as well as the proof of the easy conversion of 2-hydroxy-4-pyrrolines into pyrrole derivatives elucidate the much debated behaviour of these reactions.

INTRODUCTION

During the last twenty years the chemistry of conjugated azoalkenes has been extensively studied.[1] In particular, the reaction of these derivatives with compounds containing activated methylene groups has been shown to be capable of providing the direct synthesis of a large number of widely substituted and unusual 1-aminopyrrole derivatives.[1] However, some authors studying analogous reactions have reported the formation of dihydropyridazines.[2] More recent investigations, by means of ^{13}C-NMR and X-ray diffraction studies,[3-5] have shown these products to be 1-aminopyrroles. This misconception is ascribable to the fact that the nucleophilic attack by activated methylene compounds containing adjacent ketonic carbonyl groups on the heterodiene system of the conjugated azoalkene results in a preliminary formation of the 1,4-adduct. This addition may be followed by an intramolecular condensation in which both nitrogen atoms of the resulting hydrazone derivative could, in principle, be operative affording six-membered pyridazine-type heterocycles (see path A in Scheme 1) or five-membered heterocycles of pyrrole-type (see path B in Scheme 1). Furthermore, dihydropyridazine derivatives could subsequently rearrange into more stable pyrrole systems. Indeed, dihydropyridazines are known to be relatively unstable, while pyrroles are very stable compounds.[1]

The present study has been undertaken with a view to formulating a general strategy for the synthesis of 1-aminopyrroles by the reaction between conjugated azoalkenes and activated methylene compounds. This investigation has also been undertaken in order to tentatively elucidate the much debated behaviour of these reactions.



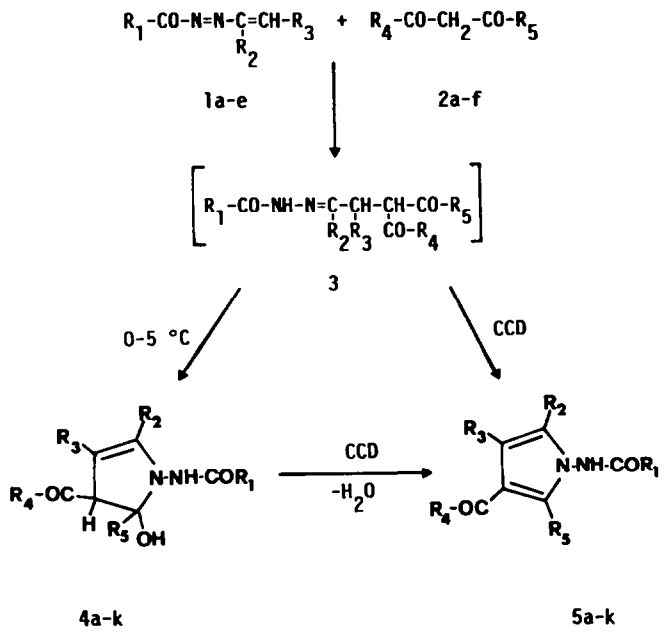
Scheme 1

RESULTS AND DISCUSSION

In the presence of copper(II) chloride dihydrate (CCD) as catalyst, the reactions of aroylazoalkenes (**1a-f**) with β-diketones (**2a-c**) and β-ketoesters (**2d-g**) directly afford 1-aroylamino-3-carbonylpyrroles (**5a-b, 5f-g, 5i**) and 1-aroylamino-3-alkoxycarbonylpyrroles (**5c-e, 5h, 5k**) respectively, whereas the related 2-hydroxy-4-pyrrolines (**4a-k**) may be shown to be present only in traces (see Scheme 2). Times, yields and melting points of the compounds **5a-k** are listed in Table 1.

In the absence of the inorganic salt, 2-hydroxy-4-pyrrolines (**4a-k**) are clearly detected as stable compounds. In fact, in some cases (**4d-f, 4i** and **4k**), these derivatives represent the main reaction product that may be readily isolated in good yields. In the remaining cases, the rate of formation of the 2-hydroxy-4-pyrrolines appears to be similar to the rate of its conversion into related 1-aminopyrrole derivatives. In all these cases, the first intermediate is assumed to be considered the 1,4-adduct (**3**) according to our previous investigations on this matter (see Scheme 2).[1] Times, yields and melting points of the compounds (**4d-f, 4i** and **4k**) are listed in Table 2.

Furthermore, the almost quantitative conversion of 2-hydroxy-4-pyrrolines (**4d-f, 4i** and **4k**) into corresponding 1-aminopyrrole derivatives (**5d-f, 5i** and **5k**) by addition of CCD has been observed. Time and yield of this conversion are shown in Table 3.



1	R_1	R_2	R_3	2	R_4	R_5
a	C_6H_5	CH_3	$COOCH_3$	a	CH_3	CH_3
b	C_6H_5	CH_3	$COOC_2H_5$	b	C_6H_5	CH_3
c	m-$CH_3C_6H_4$	CH_3	$COOCH_3$	c	C_6H_5	C_6H_5
d	m-$CH_3C_6H_4$	CH_3	$COOC_2H_5$	d	OCH_3	CH_3
e	m-ClC_6H_4	CH_3	$COOCH_3$	e	OC_2H_5	CH_3
f	$CH_2C_6H_5$	CH_3	$COOCH_3$	f	OC_2H_5	C_6H_5
				g	OC_2H_5	p-$NO_2C_6H_4$

Scheme 2

Table 1 - Time, yield, and melting points of 1-aroylamino-3-cabonylpyrroles and 1-aroylamino-3-alkoxycarbonylpyrroles **5a-k** obtained in the presence of CCD.

Azoalkene	ß-Dicarbonyl Compound	1-Aminopyrrole	Reaction time (h)	Yield[a] (%)	Mp[b] (°C)
1a	2a	5a	10	67	176-177
1b	2c	5b	0.5	83	190-191
	2d	5c	3	96	142-144
	2f	5d	0.5	83	126-128
	2g	5e	0.1	73	200-202
1c	2b	5f	2.5	81	175-177
	2c	5g	1.5	85	193-194
1d	2e	5h	4.5	87	119
1e	2b	5i	0.1	84	174-175
1f	2g	5k	1	70	168-169

[a]Yield of pure isolated product. [b]Melting points are uncorrected and occur with decomposition.

Table 2 - Time, yield, and melting points of 2-hydroxy-4-pyrrolines **4d-f**, **4i** and **4k**.

Azoalkene	ß-Dicarbonyl Compound	2-Hydroxy-4-pyrroline	Reaction time (h)	Yield[a] (%)	Mp[b] (°C)
1b	**2f**	**4d**	6	86	181-182
	2g	**4e**	1	77	199-200
1c	**2b**	**4f**	0.7	76	189-191
1e	**2b**	**4i**	0.1	80	170-172
1f	**2g**	**4k**	3	77	159-160

[a]Yield of pure isolated product. [b]Melting points are uncorrected and occur with decomposition.

Table 3 - Time and yield of the conversion of 2-hydroxy-4-pyrrolines (**4d-f**, **4i** and **4k**) into related 1-aminopyrroles (**5d-f**, **5i** and **5k**).

2-Hydroxy-4-pyrroline	1-Aminopyrrole	Reaction time (h)	Yield[a] (%)
4d	**5d**	0.3	95
4e	**5e**	18	94
4f	**5f**	0.3	93
4i	**5i**	0.3	92
4k	**5k**	18	93

[a]Yield of pure isolated product.

This fact clearly demonstrates that the effective role as intermediates in these reactions is played by these substances rather than by dihydropyridazines previously hypothesized by other authors for the same function. Although we had already postulated the formation of the 2-hydroxy-4-pyrroline intermediate arising from the internal cyclization by C=N nitrogen atom of the 1,4-adduct intermediate, our attempts to isolate this cyclic intermediate have been unsuccessful, probably because of the easy loss of the water molecule with production of the aromatic pyrrole ring.

IR and ^{1}H NMR (60 MHz) spectra confirmed the aforementioned molecular structures. Further interesting information especially on the stereochemistry of 2-hydroxy-4-pyrrolines has been obtained by high field proton NMR at 300 MHz. From this comparative study, **4e** and **4k** appear to be isomeric mixtures. This conclusion is mainly based on the fact that each compound exhibits two triplets at nearly δ =0.8 and δ =1.2 ppm both ascribable to the methyl group of the carboethoxy substituent at asymmetric C(3) atom, two singlets at δ =5.0-5.2 and δ =5.5-5.6 ppm for the hydroxy group at asymmetric C(2) atom, while **4d**, **4f** and **4i** seem to be pure isomeric forms (see Experimental). Moreover, it is well known that some conformational differences frequently occur for molecules in crystal or solution state.

An X-ray diffraction study of the compound **4e** and the related pyrrole derivative **5e** affording from the reaction between **1b** and **2g** was carried out in order to unambiguously confirm the spectral data in agreement with the assignment of the structures pictured in the Scheme 2 both for the 2-hydroxy-4-pyrrolines (**4a-k**) and 1-aminopyrroles (**5a-k**). The stereochemistry and the molecular packing of 2-hydroxy-4-pyrroline **4e** are shown in Figure 1 and 2, respectively. Hydroxy group HO(6) is linked to C(2) atom. This atom and C(3) represent two typical tetrahedral carbon atoms. In fact, the C(2)-C(3) bond distance is of 1.56(1) Å showing a pure single bond between these two atoms, while a localized double bond between C(4) and C(5) is manifested by the bond

distance of 1.33(1) Å. The sum of the bond angles around the heteroatom N(1) is close to 344°, supporting a non-perfect sp^2 hybridization for this atom. Moreover, the sum of the bond angles involving the atoms of the five-membered heterocycle is 531.5°. For these reasons, the ring is a non-planar pentagon. Intermolecular O(6)H...O(9) and intramolecular bonds O(6)H...N(7) are also revealed to be both of 2.782 Å.

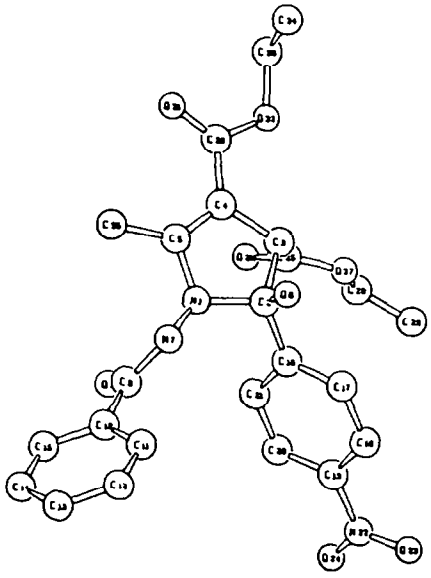


Figure 1. X-Ray crystal structure of 2-hydroxy-4-pyrroline **4e** with the atom numbering system used in the crystallographic analysis.

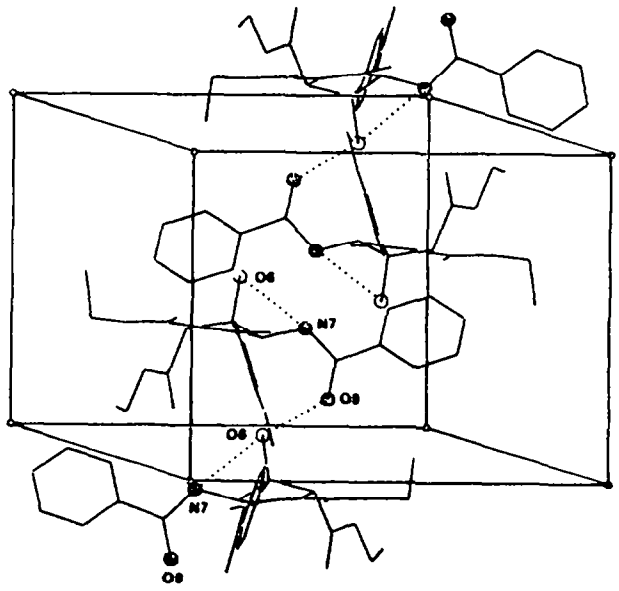


Figure 2. Molecular packing of 2-hydroxy-4-pyrroline **4e**.

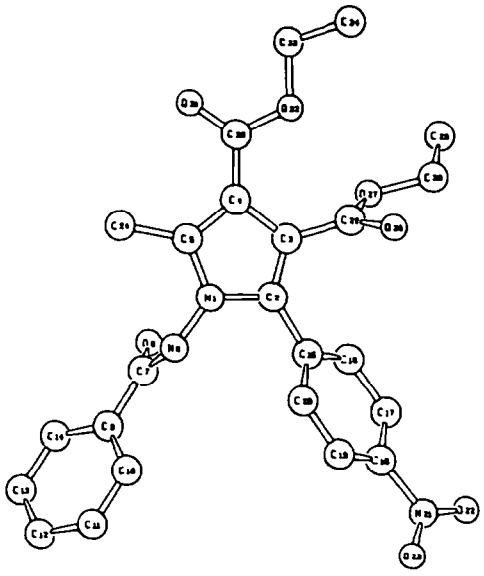


Figure 3. Crystal structure of 1-aminopyrrole **5e** with the atom numbering system used in the crystallographic analysis.

Figure 3 shows the stereochemistry of the 1-aminopyrrole **5e**. Bond lengths and angles of the pyrrole ring are in good agreement with those of our previous finding on this matter.[3,4] Indeed, in this case the C(2)-C(3) and C(4)-C(5) bond distances of 1.32(2) Å and 1.36(2) Å, respectively, indicate two double bonds between these couples of carbon atoms in the ring. In general, very similar bond distances are observed for all the atoms of the ring. The sum of the bond angles around the heteroatom N(1) is close to 360°, confirming sp^2 hybridization for this atom. In addition, the sum of the bond angles involving the atoms of the heterocycle is exactly 540°. For these reasons, the deviations from the plane for the atoms of the five-membered ring are very small.

EXPERIMENTAL

ß-Diketones and ß-ketoesters (**2**) were commercial materials and were used without further purification. Aroylazoalkens were prepared as previously reported.[6] Mps were determined in capillary tubes with a Büchi apparatus, and are uncorrected. The products often decompose at melting point. IR spectra were obtained in Nujol mull with a Perkin-Elmer 298 spectrophotometer, and ν values are expressed in cm^{-1}. ^1H NMR spectra at 60 MHz were recorded on a Varian EM-360L spectrometer in DMSO-d_6 or $CDCl_3$, while ^1H NMR spectra at 300 MHz were recorded on a Bruker CXP 300 spectrometer in CD_3CN. Chemical shifts (δ) are reported in ppm downfield from internal TMS and coupling constants (J) in Hz. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; D_2O ex, D_2O exchange. Merck precoated silica gel $60F_{254}$ plates were employed for analytical thin layer chromatography (TLC), Merck silica gel PF_{254} plates for preparative TLC, and silica gel Kieselgel 60 (0.063-0.200 mm) for column chromatography. All the compounds prepared showed a satisfactory elemental analysis (C±0.35, H±0.30, N±0.30).

General procedure for the synthesis of 2-hydroxy-4-pyrrolines (4d-f, 4i and 4k). To a stirred solution of aroylazoalkene (1 mmol) dissolved in tetrahydrofuran (1 ml) was added ß-diketone or ß-ketoester (1 mmol) and the mixture was stirred at 0-5 °C until aroylazoalkene completely disappeared, producing the relative 2-hydroxy-4-pyrroline derivative (monitored by silica gel TLC). Frequently, a precipitate was observed, and the product **4** was isolated in satisfactory

purity by filtration. Alternatively, tetrahydrofuran was removed by evaporation under reduced pressure and the residue was crystallized from methanol to provide the product **4**.

1-Benzoylamino-2-hydroxy-2-phenyl-3,4-diethoxycarbonyl-5-methyl-4-pyrroline (4d). IR 3215, 1730, 1685, 1655 cm^{-1}; ^1H NMR (CD_3CN) 0.77 (3H, t, J=7.5), 1.21 (3H, t, J=7.5), 2.33 (3H, s), 3.42 (1H, m), 3.60 (1H, m), 3.96 (1H, s), 4.12 (2H, m), 5.38 (1H, br s, D_2O ex), 7.27-7.77 (10H, m), 8.83 (1H, br s, D_2O ex) ppm.

1-Benzoylamino-2-hydroxy-2-(p-nitrophenyl)-3,4-diethoxycarbonyl-5-methyl-4-pyrroline (4e). IR 3300, 1730, 1695, 1660, 1645, 1520, 1345 cm^{-1}; ^1H NMR (CD_3CN) 0.80 (3H, t, J=7.5), 1.22 (9H, m), 2.30 (3H, s), 2.33 (3H, s), 3.41-3.70 (3H, m), 4.01 (1H, m), 4.15 (6H, m), 5.20 (1H, s, D_2O ex), 5.60 (1H, br s, D_2O ex), 7.44-8.35 (18H, m), 8.89 (1H, br s, D_2O ex), 8.94 (1H, s, D_2O ex) ppm.

1-(m-Methylbenzoylamino)-2-hydroxy-2-methyl-3-benzoyl-4-methoxycarbonyl-5-methyl-4-pyrroline (4f). IR 3280, 1690, 1655, 1610 cm^{-1}; ^1H NMR (CD_3CN) 1.58 (3H, s), 2.21 (3H, s), 2.43 (3H, s), 3.50 (3H, s), 4.11 (1H, s, D_2O ex), 4.97 (1H, s), 7.37-8.08 (9H, m), 8.84 (1H, br s, D_2O ex) ppm.

1-(m-Chlorobenzoylamino)-2-hydroxy-2-methyl-3-benzoyl-4-methoxycarbonyl-5-methyl-4-pyrroline (4i). IR 3280, 1690, 1655, 1610 cm^{-1}; ^1H NMR (CD_3CN) 1.58 (3H, s), 2.21 (3H, s), 3.50 (3H, s), 4.06 (1H, br s, D_2O ex), 4.96 (1H, s), 7.48-8.08 (9H, m), 8.89 (1H, br s, D_2O ex) ppm.

1-(Phenylacetylamino)-2-hydroxy-2-(p-nitrophenyl)-3-ethoxycarbonyl-4-methoxycarbonyl-5-methyl-4-pyrroline (4k). IR 3300, 2990, 1725, 1700, 1675, 1645, 1520, 1340 cm^{-1}; ^1H NMR (CD_3CN) 0.75 (3H, t, J=7.5), 1.19 (3H, t, J=7.5), 2.13 (3H, s), 2.19 (3H, s), 3.45 (5H, m), 3.63 (8H, m), 3.94 (1H, m), 4.14 (2H, m), 4.98 (1H, s, D_2O ex), 5.48 (1H, s, D_2O ex), 7.04-8.23 (18H, m), 8.45 (1H, br s, D_2O ex), 8.63 (1H, br s, D_2O ex) ppm.

General procedure for the synthesis of 1-aroylamino-3-carbonylpyrroles (5a-b, 5f-g, 5i), 1-aroylamino-3-alkoxycarbonylpyrroles (5c-e, 5h, 5k). To a stirred solution of aroylazoalkene (1.0 mmol) dissolved in tetrahydrofuran (1 ml) there was added ß-diketone or ß-ketoester (1 mmol). For the synthesis of 1-aminopyrroles **5a-k**, copper(II) chloride dihydrate (0.05 mmol) was added to the mixture. In all cases, the reaction was allowed under magnetic stirring at room temperature until aroylazoalkene had completely reacted, directly affording the respective 1-aminopyrrole derivative (monitored by silica gel TLC). This product may be isolated and purified with same metodologies as for 2-hydroxy-4-pyrroline derivatives **4** described above. Otherwise, preliminar purification of the reaction mixture by chromatography on a silica gel column may be necessary (elution with cyclohexane-ethyl acetate mixtures). In any case, further purification of the product **5** may be obtained by recrystallization from methanol.

1-Benzoylamino-2,5,-dimethyl-3-acetyl-4-methoxycarbonylpyrrole (5a). IR 3200, 1710, 1690, 1675 cm^{-1}; ^1H NMR (DMSO-d_6) 2.15 (3H, s), 2.28 (3H, s), 2.35 (3H, s), 3.77 (3H, s), 7.60-8.13 (5H, m), 11.82 (1H, br s, D_2O ex) ppm.

1-Benzoylamino-2-phenyl-3-benzoyl-4-ethoxycarbonyl-5-methylpyrrole (5b). IR 3260, 1705, 1685, 1655 cm^{-1}; ^1H NMR (DMSO-d_6) 0.82 (3H, t, J=7.0), 2.48 (3H, s), 3.89 (2H, q, J=7.0), 7.35 (5H, s), 7.47-8.03 (10H, m), 11.93 (1H, br s, D_2O ex) ppm.

1-Benzoylamino-2,5-dimethyl-3-methoxycarbonyl-4-ethoxycarbonylpyrrole (5c). IR 3225, 1690 cm^{-1}; ^1H NMR (DMSO-d_6) 1.25 (3H, t, J=7.0), 2.23 (6H, s), 3.73 (3H, s), 4.21 (2H, q, J=7.0), 7.58-8.13 (5H, s), 11.78 (1H, br s, D_2O ex) ppm.

1-Benzoylamino-2-phenyl-3,4-diethoxycarbonyl-5-methylpyrrole (5d). IR 3265, 1725, 1700, 1660 cm^{-1}; ^1H NMR (DMSO-d_6) 1.12 (3H, t, J=7.0), 1.27 (3H, t, J=7.0), 2.37 (3H, s), 3.93-4.42 (4H, m), 7.43 (5H, s), 7.50-7.93 (5H, m), 11.82 (1H, br s, D_2O ex) ppm.

1-Benzoylamino-2-(p-nitrophenyl)-3,4-diethoxycarbonyl-5-methylpyrrole (5e). IR 3160, 1715, 1665, 1515, 1340 cm^{-1}, ^1H NMR (DMSO-d_6) 1.20 (3H, t, J=7.0), 1.33 (3H, t, J=7.0), 2.47 (3H, s), 4.10-4.57 (4H, m), 7.72-8.65 (9H, m), 12.37 (1H, br s, D_2O ex) ppm.

1-(m-Methylbenzoylamino)-2,5-dimethyl-3-benzoyl-4-methoxycarbonylpyrrole (5f). IR 3175, 1710, 1695, 1630 cm^{-1}; ^1H NMR (DMSO-d_6) 2.08 (3H, s), 2.35 (3H, s), 2.43 (3H, s), 3.22 (3H, s), 7.45-7.85 (9H, m), 11.77 (1H, br s, D_2O ex) ppm.

1-(m-Methylbenzoylamino)-2-phenyl-3-benzoyl-4-methoxycarbonyl-5-methylpyrrole (5g). IR 3245, 1715, 1660, 1655 cm^{-1}; ^1H NMR (DMSO-d_6) 2.37 (3H, s), 2.47 (3H, s), 3.40 (3H, s), 7.37 (5H, s), 7.47-7.87 (9H, m), 11.93 (1H, br s, D_2O ex) ppm.

1-(p-Methylbenzoylamino)-2,5-dimethyl-3,4-diethoxycarbonylpyrrole (5h). IR 3250, 1705, 1685, 1675 cm^{-1}; ^1H NMR (DMSO-d_6) 1.27 (6H, t, J=7.0), 2.25 (6H, s), 2.43 (3H, s), 4.22 (4H, q, J=7.0), 7.47-7.98 (4H, m), 11.89 (1H, br s, D_2O ex) ppm.

1-(p-Chlorobenzoylamino)-2,5-dimethyl-3-benzoyl-4-methoxycarbonylpyrrole (5i). IR 3170, 1695, 1625 cm^{-1}; ^1H NMR (DMSO-d_6) 2.10 (3H, s), 2.37 (3H, s), 3.23 (3H, s), 7.47-8.10 (9H, m), 11.98 (1H, br s, D_2O ex) ppm.

1-(Phenylacetylamino)-2-(p-nitrophenyl)-3-ethoxycarbonyl-4-methoxycarbonyl-5-methylpyrrole (5k). IR 3190, 1715, 1670, 1520, 1350 cm^{-1}; ^1H NMR (DMSO-d_6) 1.10 (3H, t, J=7.0), 2.32 (3H, s), 3.48 (2H, s), 3.80 (3H, s), 4.13 (2H, q, J=7.0), 7.27 (5H, s), 7.55 (2H, d, J=9.0), 8.19 (2H, d, J=9.0), 11.52 (1H, br s, D_2O ex) ppm.

General procedure for the conversion of 2-hydroxy-4-pyrrolines (4d-f, 4i and 4k) into 1-aroylamino-3-carbonylpyrroles (5f and 5i) and 1-aroylamino-3-alkoxycarbonylpyrroles (5d-e and 5k). To a stirred solution of 2-hydroxy-4-pyrroline (1 mmol) dissolved in tetrahydrofuran (2 ml) was added copper(II) chloride dihydrate (0.05 mmol), and the mixture was allowed under magnetic stirring at room temperature until the completion of the reaction (monitored by silica gel TLC). The conversion was almost quantitative, and the product may be isolated and purified with same methodologies as for 1-aminopyrrole derivatives described above.

X-Ray analysis of compounds 4e and 5e. Intensity data were collected by a CAD4 diffractometer using $\omega/2\vartheta$ scan; ϑ range $2.5° \leq \vartheta \leq 25°$. MoK α radiation λ=0.7107 Å. Diffraction intensities were measured with a 1.0 deg. scan width and a scan speed variable between 0.7-8.0 deg min^{-1}. The unit-cell parameters were determined by a least-squares refinement on 25 independent 2ϑ values.

Crystal data of compound 4e. $C_{24}H_{25}N_3O_8$, MW=483.47, monoclinic, space group $P2_1/n$, a=12.761(5) Å, b=10.135(4) Å, c=20.412(7) Å, β=103.6(1)°, Z=4, D_c=1.25 g cm^{-3}, V=2565.3 $Å^3$. Of 3026 independent reflections, 1697 having $I > 1.5\sigma$ (I) were considered observed.

Crystal data of compound 5e. $C_{24}H_{23}N_3O_7$, MW=465.47, monoclinic, space group $P2_1/a$, a=9.519(5) Å, b=21.916(8) Å, c=11.904(6) Å, β=99.2(1)°, Z=4, D_c=1.26 g cm^{-3}, V=2451.4 $Å^3$. Of 3171 independent reflections, 1439 having $I > 2.5\sigma$ (I) were considered observed.

Structure determination and refinement. The structures were solved by direct methods and Fourier techniques, using the SHELX 76[7] program and SHELX 86[8] program package. Refinement proceeded by block-diagonal least-squares methods using anisotropic thermal parameters for all non-hydrogen atoms. The phenyl rings were treated as rigid bodies of D6h symmetry with C-C distances fixed at 1.395 Å and all hydrogen atoms were calculated geometrically (C-H 1.08 Å). The final agreement index was R=0.078 for **4e** and R=0.075 for **5e**, respectively. The atomic co-ordinates for this work are available on request from the director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this paper.

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