Reactions of β-Dicarbonyl Compounds with Acyl Cyanides Catalyzed or Promoted by Metal Centres in the Homogeneous Phase

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The C–C bond-forming reaction between β-dicarbonyl compounds and acyl cyanides is catalyzed by nickel acetylacetonate or promoted by tin tetrachloride. Thus, β-diketones react with acyl cyanides in the presence of catalytic amounts of [Ni(acac)$_2$] to give β-enamino diketones **3**. β-Enamino keto esters **8** or β-enamino diesters **9** are obtained in the reactions of methyl acetoacetate or methyl malonate with acyl cyanides in the presence of stoichiometric amounts of $SnCl_4$. The reactions of acyl cyanides with methyl malonate also afford furanone derivatives **10**, whose structure has been determined, in one case, by a single-crystal X-ray analysis. β-Keto amides react with acyl cyanides to give pyrrolidine derivatives **13** both under catalytic conditions and stoichiometric conditions where an equimolar equivalent of promoter was used.

In recent years we have been interested in the reactions of β-dicarbonyl compounds with nitriles.[1] In the presence of metal acetylacetonates as catalysts[2–6] or of tin(IV) chloride as promoter,[7,8] these reactions give β-enamino diones, which result from the formation of a new carbon–carbon bond between the methylene group of the β-dicarbonyls and the cyano group of the nitriles.

Acyl cyanides, an interesting class of nitriles particularly useful in organic synthesis,[9] can react with nucleophiles in different ways. The more common reaction pathway involves attack of the nucleophile at the carbonyl group with elimination of hydrogen cyanide, so that acyl cyanides behave as mild acylating agents. Nucleophiles such as water, alcohols, mercaptans, amines, Grignard reagents and lithium enolates react in this way. In particular, the sodium salt of β-diketones gives α-acylated-β-diketones derived from C-acylation of the intercarbonylic methylene group.[10] Only a few examples of attack of nucleophile at the cyano group to give addition products have been reported, the reaction of acyl cyanides with H_2S being the most important.[11] Thus, as a rule, acyl cyanides are unstable under the basic conditions usually required in non radical C–C bond-forming reactions.

However, as reported in a preliminary communication, [Ni(acac)$_2$] is able to catalyze the reaction of β-diketones **1a–c** with benzoyl cyanide **2a** to give the desired β-enamino diketones **3a–c**, whose structure was demonstrated by an X-ray analysis (for **3b**).[12]

In the present paper we report the results obtained in the metal-catalyzed (or promoted) reactions of β-diketones, β-keto esters, β-diesters and β-keto amides with the aromatic acyl cyanides **2a–c** and with acetyl cyanide **2d**.

Results

The reaction of β-dicarbonyls with acyl cyanides, in the presence of catalytic amounts of [Ni(acac)$_2$] or of stoichiometric amounts of tin(IV) chloride, affords compounds resulting from carbon–carbon bond formation between the methylene group of β-dicarbonyls and the cyano group of nitriles. The choice of the metal centre is very important with respect to the nature of the products and to their yields, so that optimum experimental conditions are required to obtain the desired β-enamino diones.

The catalytic reactions were carried out in the presence of [Ni(acac)$_2$] (2–4% mol) as catalyst in chlorinated solvents, generally 1,2-dichloroethane, with heating at reflux for 4–6 h (method A).[12]

The stoichiometric reactions were carried out in the presence of an equimolar amount of tin(IV) chloride either in toluene or in ethyl acetate with heating at reflux for 3–5 h or in ethyl acetate at room temperature for 24 h. The reaction mixture was finally treated with 20% aqueous sodium carbonate (pH *ca.* 10) for 30 min and extracted with ethyl acetate to give the organic products (method B).[7]

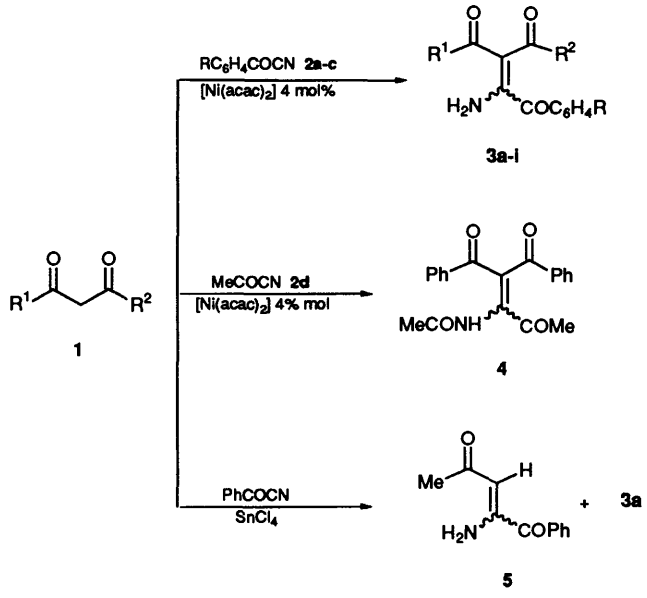
Reaction of β-Diketones with Acyl Cyanides.—The catalytic reactions (method A) of β-diketones **1a–c** with benzoyl cyanide **2a**, *p*-toluoyl cyanide **2b** and *p*-methoxybenzoyl cyanide **2c** provided the β-enamino diketones **3a–i** in good yields.

The catalytic reactions of β-diketones **1a–c** with acetyl cyanide **2d** generally gave complex reaction mixtures. Only in the reaction of dibenzoylmethane **1c** was it possible to isolate the *N*-acetylated enamino diketone **4** in low yield.

When the reaction of **1a** with benzoyl cyanide **2a** was carried out in the presence of tin(IV) chloride (method B) a complex reaction mixture was obtained, from which only small amounts of the β-enamino diketone **3a** could be detected, the main product being the β-enamino ketone **5**.[7]

Reaction of β-Keto esters and β-Diesters with Acyl Cyanides.—When β-keto esters and β-diesters were treated with benzoyl cyanide in catalytic conditions no reaction was observed. On the other hand when the reactions of methyl acetoacetate **6** with aroyl cyanides **2a–c** were carried out in the presence of tin(IV) chloride with heating at reflux for 3 h in toluene (method B) the β-enamino keto esters **8a–c** were obtained in good yields.

Moreover, the reaction of methyl malonate **7** with benzoyl cyanide **2a**, carried out in toluene at reflux, provided good yields of the β-enamino diester **9a**. When the same reaction was carried out in ethyl acetate at room temperature for 24 h or heating at reflux for 5 h, instead of compound **9a**, the 2,5-dihydrofuranone derivative **10a** was obtained. In the reaction of methyl malonate **7** with acetyl cyanide **2d**, only the furanone derivative **10b** was obtained when the reaction was carried out both with heating at reflux in toluene or in ethyl acetate at room

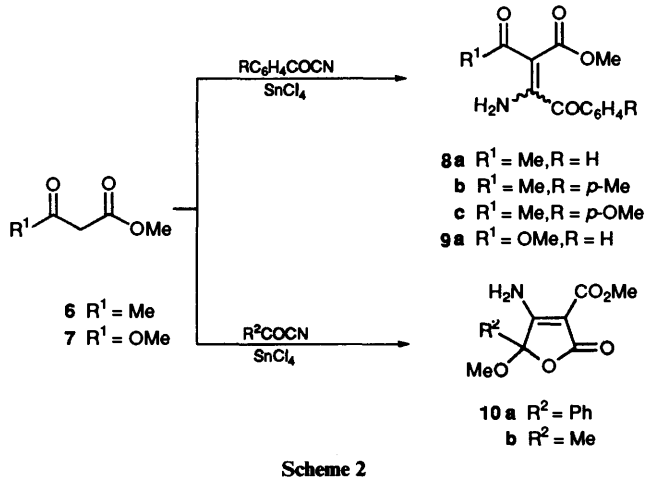


1a $R^1 = R^2 = Me$
b $R^1 = Me, R^2 = Ph$
c $R^1 = R^2 = Ph$
2a R = H
b R = *p*-Me
c R = *p*-OMe

3a $R^1 = R^2 = Me, R = H$
b $R^1 = Me, R^2 = Ph, R = H$
c $R^1 = R^2 = Ph, R = H$
d $R^1 = R^2 = Me, R = p$-Me
e $R^1 = Me, R^2 = Ph, R = p$-Me
f $R^1 = R^2 = Ph, R = p$-Me
g $R^1 = R^2 = Me, R = p$-OMe
h $R^1 = Me, R^2 = Ph, R = p$-OMe
i $R^1 = R^2 = Ph, R = p$-OMe

Scheme 1

temperature. Its structure has been determined by a single-crystal X-ray analysis (see later). Compound **10a** could also be obtained by heating under reflux the β-enamino diester **9a** in ethyl acetate for 3 h in the presence of tin(IV) chloride or by treating a solution of **9a** in ethyl acetate with gaseous hydrogen chloride.

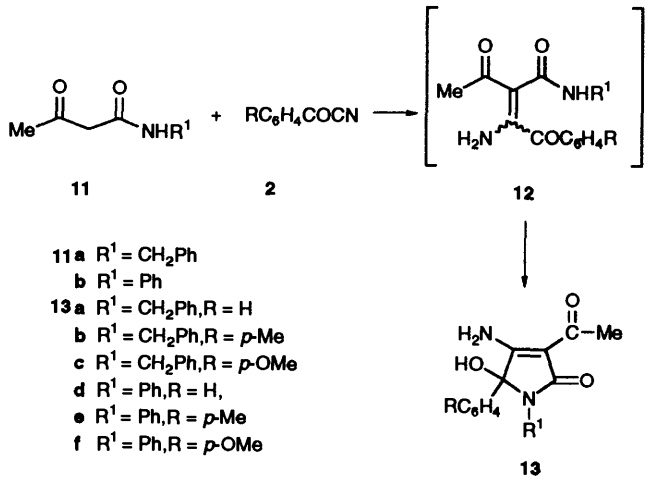


Scheme 2

Reactions of β-Keto Amides.—The β-keto amides **11a–b** react with aryl cyanides **2a–c** under catalytic conditions to give the pyrrolidinone derivatives **13a–f**: the yields are generally low and in the range 5–30%.

Similar reactions carried out in the presence of stoichiometric amounts of tin(IV) chloride gave increased yields of compound **13a–f** (60–95%).

In these reactions the β-enamino keto amides **12** cannot be isolated owing to their rapid intramolecular cyclisation to the pyrrolidine derivatives **13**.



11a $R^1 = CH_2Ph$
b $R^1 = Ph$
13a $R^1 = CH_2Ph, R = H$
b $R^1 = CH_2Ph, R = p$-Me
c $R^1 = CH_2Ph, R = p$-OMe
d $R^1 = Ph, R = H$,
e $R^1 = Ph, R = p$-Me
f $R^1 = Ph, R = p$-OMe

Scheme 3

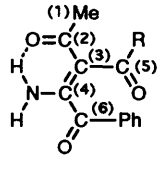
Table 1 NMR chemical shifts for β-enamino diones in solution and in the solid state

	3a solid state	3a in [$^2H_6$]DMSO	3b solid state	3b in [$^2H_6$]DMSO form A	3b in [$^2H_6$]DMSO form B
C(1)	31.5	30.6	34.3	29.8	31.0
C(7)	32.3	32.0			
C(3)	109.9	111.3	112.0	109.8	109.7
C(4)	172.1	168.8	ca. 168	166.7	166.1
C(6)	191.9	189.0	190.3	189.9	190.4
C(2)	194.9	194.9	197.5[a]	194.5[a]	194.4[a]
C(5)	201.2	197.7	198.4[a]	195.5[a]	196.9[a]
C(Ph)	126.6–137.0	127.7–135.1	126.0–142.7	127.8–141.6	
H(Me)		2.28		1.55	1.77
H(Me)		2.47			
NH		9.40		9.36	9.36
NH		10.67		9.78	10.65
H(Ph)		7.32–7.82		7.37–7.87	

[a] Tentative attributions, which can be interchanged.

NMR Spectra in Solution and in the Solid State.—Accurate NMR investigations of compounds **3a,b**, including high-resolution solid-state ^{13}C CP/MAS NMR and specific ^{13}C labelling allowed a safe assignment of the various resonances and reasonable predictions on the conformation of the compounds in the two phases.

The results are consistent with structures **3**, which also indicate the numbering scheme adopted in Table 1.



3a R = Me [$C^{(7)}$]
b R = Ph

The compounds are characterized by three distinct carbonyl resonances, thus indicating the non-equivalence of the CO carbon nuclei. The attribution to C(6) of the resonance around 190 ppm is supported by its selective ^{13}C enrichment (for **3a**)

Table 2 Selected bond lengths (Å) and angles (°) for the furan derivative **10b** (esd's)

O(1)–C(2)	1.212(2)	C(1)–O(2)–C(2)	116.4(1)
O(2)–C(1)	1.448(2)	C(6)–O(4)–C(8)	115.6(2)
O(2)–C(2)	1.352(2)	C(4)–O(5)–C(6)	110.5(2)
O(3)–C(4)	1.214(2)	O(1)–C(2)–O(2)	123.1(2)
O(4)–C(6)	1.397(2)	O(2)–C(2)–C(3)	110.7(1)
O(4)–C(8)	1.436(2)	O(1)–C(2)–C(3)	126.2(2)
O(5)–C(4)	1.377(2)	C(2)–C(3)–C(5)	128.7(2)
O(5)–C(6)	1.447(2)	C(2)–C(3)–C(4)	123.5(1)
N(1)–C(5)	1.322(2)	C(4)–C(3)–C(5)	107.8(2)
C(2)–C(3)	1.458(2)	O(5)–C(4)–C(3)	109.7(1)
C(3)–C(4)	1.450(2)	O(3)–C(4)–C(3)	131.2(2)
C(3)–C(5)	1.390(2)	O(3)–C(4)–O(5)	119.1(2)
C(5)–C(6)	1,531(2)	N(1)–C(5)–C(3)	131.4(2)
C(6)–C(7)	1.526(2)	C(3)–C(5)–C(6)	108.5(1)
		N(1)–C(5)–C(6)	120.0(1)
		O(5)–C(6)–C(5)	103.5(1)
		O(4)–C(6)–C(5)	112.8(2)
		O(4)–C(6)–O(5)	109.7(2)
		C(5)–C(6)–C(7)	113.9(2)
		O(5)–C(6)–C(7)	108.9(1)
		O(4)–C(6)–C(7)	107.9(2)

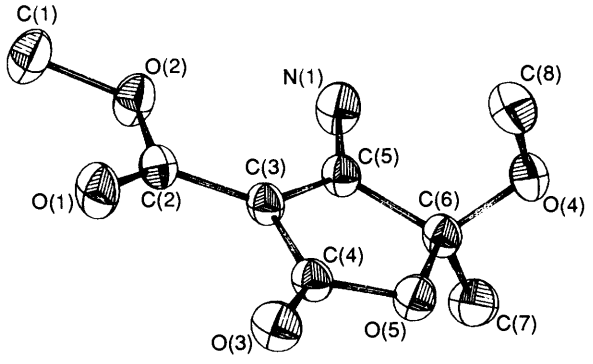


Fig. 1 ORTEP view of furan derivative **10b** with numbering system used in the tables of data

and that of C(2) and C(5) (194.4–201.2 ppm) is based on the obvious assumption that hydrogen bonding reduces the double-bond character of the involved carbonyl, so moving its chemical shift to lower values. The attribution is, however, tentative for **3b**, because of closeness of the two values and of the change of one substituent from methyl to phenyl. The methyl resonances in **3a** [C(1) and C(7)] are determined on the basis of the selective decoupling technique. The C–N resonance is almost undetectable in the solid state since it appears as a very broad signal (around 170 ppm), which becomes sharp only on ^{13}C enrichment. The spectra are very similar in solution and in the solid state, which suggests the same configuration exists in both; this has weak hydrogen bonding between one keto group and the amino group as already proved by an X-ray single crystal analysis on **3b**.[12] A variable-temperature study on **3a** has shown that the two double resonances due to the methyl and amino hydrogens coalesce at 110 °C to single peaks at 2.31 and 9.66 ppm, respectively, thus indicating free rotation through the C–N and C(3)–C(4) bonds at this temperature. The solution spectrum of **3b** in [$^2H_6$]DMSO shows the existence of two species in an equilibrium ([form A]/[form B] *ca.* 0.4) slow on the NMR time-scale at room temperature but fast enough at 95 °C to give rise to single signals for the methyl (1.73 ppm) and amino (9.52 ppm) hydrogens. The similarity of the resonance pattern for the two forms and the presence, in both cases, of a couple of NH signals, seems to indicate the presence of two isomers in which hydrogen bonding may involve the keto oxygen of an acetyl or of a benzoyl group.

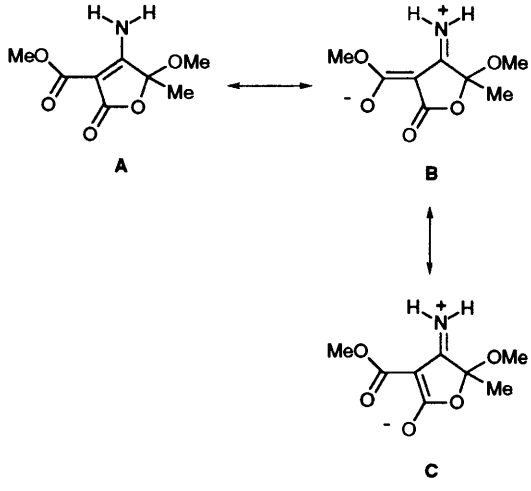
The NMR data for the other compounds are reported in the Experimental section and clearly indicate that all β-enamino diones adopt, in solution, the conformation described above, characterized at room temperature by a hydrogen bond between the amino and one keto group, without any evidence of a keto-enolic isomerism.

Infrared Spectra of the β-Enamino Diones **3a–i**.—The spectra are characterized by two bands in the range 3320–3140 cm^{-1} attributable to the N–H stretching and by a series of absorptions between 1692 and 1568 cm^{-1}. An FT-IR study on **3a**, including 99% ^{13}C enrichment of the C(4)–N and C(6)=O carbon atoms, has revealed that the band at 1663 cm^{-1} is due to the benzoyl CO stretching, whereas those at 1631 and 1565 cm^{-1} can be tentatively attributed to the carbonyl stretching of the two acetyl groups, the lower frequency value being related to the group involved in the hydrogen bond. The peak at 1594 cm^{-1} should be due to conjugated C=C or phenyl vibrations, whereas the rather high frequency of the C–N stretching is at 1417 cm^{-1}. In general, the IR data for the β-enamino diones (see Experimental section) support the molecular structure depicted above, where π-electron delocalization reduces the double bond order of the C=O groups.

Mass Spectra of Compounds **3a–c**.—The electron impact mass spectra of the compounds shows in the three examined cases the presence of the parent ion, so indicating a good thermal stability of the compounds. More important fragmentations involve release in the gas phase of the methyl, acetyl, phenyl and benzoyl groups and for **3b** and **3c** the peak due to the benzoyl fragment being the most intense.

X-Ray Structure of Compound **10b**.—An ORTEP view of the molecule is shown in Fig. 1 and Table 2 reports selected bond lengths and angles.

The furan ring scarcely deviates from planarity (d_{max} 0.004 Å), despite the limited bond delocalization expected in the presence of the C(6) sp^3 hybridized carbon atom. Most bond length and bond angle values in the ring are accounted for on the basis of isolated bonds. An extended resonance, however, involves the N(1)–C(5)–C(3) enamino group so that the carbon–carbon (1.390(2) Å) and carbon–nitrogen (1.322(2) Å) distances are, respectively, enhanced and reduced, compared with the values usually found for double C(sp^2)–C(sp^2) (1.32 Å) and single C(sp^2)–N bonds (1.38 Å).[13] Moreover, the amino hydrogen atoms lie approximately in the plane defined by the N(1)–C(5)–C(3)–C(2)–O(2) atoms (d_{max}0.05 Å) with a H(1)–N(1)–H(2) angle of 120(2)°. These observations indicate that the molecular structure of compound **10b** is represented by the Lewis structures **A**, **B** and **C**.



The short C(6)–O(4) distance of 1.397(2) Å should also be noted. The usual values for single C(sp^3)–O bond are, in fact, around 1.43 Å,[13] as indeed found for the C(8)–O(4) and C(1)–O(2) bonds.

Both intramolecular and intermolecular hydrogen bonds are present [N(1)–O(2) = 2.814(3) and N(1)–O(3) = 2.912(3) Å, respectively]. One hydrogen atom of the amino group strongly interacts with the methoxy oxygen [H(1)···O(2) = 2.18(2) Å] of the same molecule and the second one with an external keto group [H(2)···O(3) = 2.02(3) Å]. The molecules of the compound are so ordered in infinite chains.

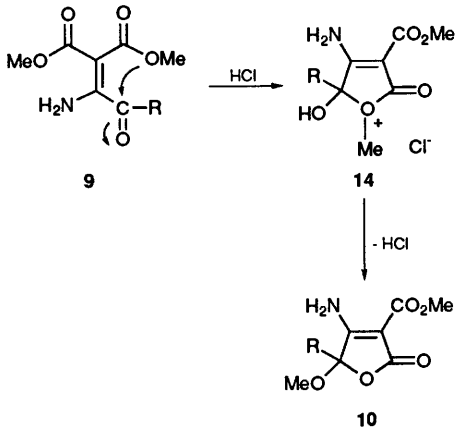
Discussion

The results obtained demonstrate that the use of metal centres makes possible a C–C bond-forming reaction not feasible under the usual basic conditions. Furthermore, the catalytic and the stoichiometric approaches can be complementary in the synthesis of the β-enamino dione derivatives **3**, **8** and **9** and of the pyrrolidinone derivatives **13**. While [Ni(acac)$_2$] gives better results than tin(IV) chloride in the reaction of β-diketones with acyl cyanides, the tin(IV) chloride stoichiometric approach is much more efficient in the reactions of β-keto esters, β-diesters and β-keto amides.

Mechanisms for the catalytic and stoichiometric reactions have been proposed earlier[8,14] and involve the coordination of the β-dicarbonyl compound and of the cyano group of the nitrile to the metal centre. The main difference between the two kinds of reactions lies in the fact that metal acetylacetonates catalyze the reaction, while tin(IV) chloride gives a stable complex with the final product, so preventing any catalytic process.

The main feature of these reactions is that both [Ni(acac)$_2$] and tin(IV) chloride increase, by coordination, the electrophilicity of the cyano group of the nitriles. This reverses the normal chemical reactivity of acyl cyanides towards β-dicarbonyls with consequent attack at the cyano group instead of at the carbonyl group. The compounds so obtained are C–C addition products of β-dicarbonyls with nitriles instead of α-acylated-β-dicarbonyls.[10]

A possible mechanism for the formation of the furanone derivatives **10** could imply the cyclisation promoted by hydrogen chloride of the β-enamino diester **9** to a cyclic oxonium ion **14** with subsequent methylation of the hydroxy group.



9 **14** **10**

Experimental

Melting points were determined on open capillary tubes on a Büchi apparatus and are uncorrected. IR spectra were taken on a Perkin-Elmer 157G or on a Bruker IFS 66 FT IR spectrometer. Samples studied were in KBr or crystalline polyethylene pellets. NMR spectra were recorded on a Bruker AC (200 MHz) spectrometer. Chemical shifts are given in ppm (δ), and coupling constants (J) are in Hz. The high-resolution solid-state ^{13}C NMR measurements were performed on a Bruker AM 250 (250 MHz) spectrometer with the experimental conditions described in ref. 15. Mass spectra were performed on a VG Micromass 16F spectrometer.

p-*Toluoyl Cyanide* **2b**.—To a solution of *p*-toluoyl chloride (1.71 cm^3, 13 mmol) in benzene (20 cm^3) NaCN (760 mg, 15.6 mmol) and 18-crown-6 (130 mg) were added. The reaction mixture was stirred at room temperature under nitrogen for 24 h and then diluted with diethyl ether. The suspension was filtered and the solvent was removed under reduced pressure to give a red oil which was purified by distillation (0.1 mmHg, 150 °C): this afforded colourless crystals (1.3 g, 72%), m.p. 47–50 °C (lit.,[16] m.p. 49 °C); $\delta_H(CDCl_3)$ 2.49 (s, 3 H, Me), 7.40 (d, J 8.2, 2 H, Ar) and 8.03 (d, J 8.2, 2 H, Ar).

p-*Methoxybenzoyl cyanide* **2c**. This compound, obtained according to the procedure described for **2b**, formed colourless crystals (87%), m.p. 55–57 °C (lit.,[16] m.p. 59 °C); $\delta_H(CDCl_3)$ 3.95 (s, 3 H, OMe), 7.05 (d, J 8.9, 2 H, Ar) and 8.9 (d, J 8.9, 2 H, Ar).

Benzoyl cyanide **2a**: ^{13}C-*enriched at* CO(Ph) *or at the* CN *groups*. These compounds were prepared according to procedure described for **2b**, treating Ph^{13}COCl with KCN or PhCOCl with K^{13}CN, respectively.

Reactions of β-Dicarbonyl Compounds with Acyl Cyanides: General Procedures.—Method A: in the presence of catalytic amounts of [Ni(acac)$_2$]. To a solution of the β-dicarbonyl compound (4 mmol) in 1,2-dichloroethane (2 cm^3) acyl cyanide (4.8 mmol) and [Ni(acac)$_2$] (0.16 mmol) were added. The reaction mixture was heated on an oil-bath at 60 °C under a nitrogen atmosphere for 3 h and then treated with diethyl ether. The crystals which formed were filtered off and the solution was concentrated to dryness to give a crude product, which was purified by flash chromatography on silica gel (eluent: ethyl acetate–light petroleum, 1:2).

Method B: in the presence of stoichiometric amounts of tin(IV) *chloride*. To a solution of the β-dicarbonyl compound (4 mmol) in toluene or in benzene (4 cm^3) acyl cyanide (4.8 mmol) and tin(IV) chloride (6 mmol) were added. The reaction mixture was heated under reflux in a nitrogen atmosphere for 3 h, cooled at room temperature and then evaporated under reduced pressure. The crystals which formed were treated with ethyl acetate (20 cm^3) and a saturated aqueous Na_2CO_3 (pH *ca.* 10; 20 cm^3) and the resulting mixture was stirred at room temperature for 0.5 h. The two layers were filtered through Celite and separated. The aqueous layer was extracted again with ethyl acetate (2 × 25 cm^3) and the combined extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to yield a crude product which was purified by flash chromatography on silica gel (eluent: ethyl acetate–light petroleum, 1:2).

Alternatively, the reaction was carried out in ethyl acetate with stirring at room temperature for 24 h or heating under reflux for 5 h.

3-*Acetyl*-2-*amino*-1-*phenylpent*-2-*ene*-1,4-*dione* **3a**. This compound, obtained by treating acetylacetone **1a** with benzoyl cyanide **2a** according to method A, formed yellow crystals, m.p. 176–179 °C (chloroform–light petroleum) (64%). A similar procedure was adopted for the ^{13}C enriched compounds starting from Ph^{13}COCN or PhCO^{13}CN (Found: C, 67.6; H, 5.8; N, 6.0. $C_{13}H_{13}NO_3$ requires C, 67.5; H, 5.7; N, 6.1); FT-IR (KBr and polyethylene pellets, in bold most significant changes on ^{13}CO or ^{13}CN enrichment) ν_{max}/cm^{-1} 3270, 3130, **1663 (1634 ^{13}CO)**, 1631, 1594, 1565, 1494, 1451, **1417 (1396 ^{13}CN)**, 1406,

1368, 1359, 1316, 1278, **1224** (**1217** ^{13}**CO**), 1182, 1158, 1102, 1079, 1043, 1033, 1025, 1010, 1001, **972** (**958** ^{13}**CO**), 962, 801, 784, 770, 738, 716, 695, 658, 632, 618, 588, 577, 494, 490, 477, 430, 412, 367, 349, 339, 319, 283, 234, 174 and 111; for ^{1}H and ^{13}C NMR spectra see Table 1; *m/z* (% relative intensity) [identity]: 231 (22) [L = $C_{13}H_{13}NO_3^+$], 216 (12) [L-Me], 188 (40) [L-MeCO], 174 (14), 154 (7) [L-Ph], 146 (10), 126 (50) [L-PhCO], 105 (86) [PhCO], 84 (74), 77 (77) [Ph] and 43 (100) [MeCO].

2-*Amino*-3-*benzoyl*-1-*phenylpent*-2-*ene*-1,4-*dione* **3b**. This compound was obtained by treating benzoylacetone **1b** with benzoyl cyanide **2a** in the molar ratio 1:1.7 according to the method A: the reaction mixture was heated at reflux for 10 h to give yellow crystals, m.p. 134–136 °C (77%) (Found: C, 73.5; H, 5.4; N, 4.9. $C_{18}H_{15}NO_3$ requires C, 73.7; H, 5.1; N, 4.8); ν_{max}(KBr)/cm^{-1} 3320, 3150, 1690, 1630, 1600, 1580, 1570 and 1260; for ^{1}H and ^{13}C NMR spectra see Table 1; *m/z* (% relative intensity) [identity]: 293 (45) [L = $C_{18}H_{15}NO_3^+$], 278 (6) [L-Me], 250 (37) [L-MeCO], 216 (6) [L-Ph], 188 (31) [L-PhCO], 146 (50), 105 (100) [PhCO], 77 (67) [Ph] and 43 (15) [MeCO].

2-*Amino*-3-*benzoyl*-1,4-*diphenylbut*-2-*ene*-1,4-*dione* **3c**. This compound was obtained by treating dibenzoylmethane with benzoyl cyanide (molar ratio 1:1.5) according to method A: the reaction mixture was heated under reflux for 6 h to afford colourless crystals, m.p. 212–214 °C (ethyl acetate–light petroleum) (62%) (Found: C, 77.4; H, 4.8; N, 4.1. $C_{23}H_{17}NO_3$ requires C, 77.7; H, 4.8; N, 3.9); ν_{max}(KBr)/cm^{-1} 3310, 3180, 1695, 1630, 1570 and 1280; δ_H([$^2H_6$]DMSO) 7.06–7.94 (m, 15 H, 3 Ph), 9.46 (br, 1 H, NH) and 10.14 (br, 1 H, NH); δ_C([$^2H_6$]DMSO) 107.10 (s, C-3), 127.06 (d, *J* 161.1, Ph), 127.17 (d, *J* 161.3, Ph), 127.33 (d, *J* 161.2, Ph), 127.77 (d, *J* 160.4, Ph), 127.90 (d, *J* 160.3, Ph), 128.27 (d, *J* 163.7, Ph), 130.07 (d, *J* 146.0, Ph), 130.43 (d, *J* 146.4, Ph), 133.11 (d, *J* 134.1, Ph), 134.10 (s, Ph), 139.82 (s, Ph), 140.94 (s, Ph), 166.38 (s, C-2), 190.08 (s, CO), 192.77 (s, CO) and 194.19 (s, CO); *m/z* (% relative intensity) [identity]: 355 (32) [L = $C_{23}H_{17}NO_3^+$], 250 (19) [L-PhCO], 223 (14), 105 (100) [PhCO] and 77 (50) [Ph].

3-*Acetyl*-2-*amino*-1-p-*tolylpent*-2-*ene*-1,4-*dione* **3d**. This compound, obtained by treating acetylacetone **1a** with toluoyl cyanide **2a** according to method A, formed yellow crystals, m.p. 148–150 °C (56%) (Found: C, 68.4; H, 5.9; N, 5.9. $C_{14}H_{15}NO_3$ requires C, 68.6; H, 6.2; N, 5.7); ν_{max}(KBr)/cm^{-1} 3280, 3180, 1670, 1640, 1580, 1360, 1310 and 1270; δ_H($CDCl_3$) 2.24 (s, 3 H, Me), 2.38 (s, 3 H, Me), 2.42 (s, 3 H, Me), 7.1 (br, 1 H, NH), 7.18 (d, *J* 8.0, 2 H, Ar), 7.61 (d, *J* 8.0, 2 H, Ar) and 10.95 (br, 1 H, NH); δ_C($CDCl_3$) 21.62 (q, *J* 122.8, Me), 30.67 (q, *J* 128.2, Me), 31.59 (q, *J* 127.9, Me), 112.37 (s, C-3), 128.18 (d, *J* 160.0, Ar), 129.33 (d, *J* 158.7, Ar), 131.75 (s, Ar), 144.40 (s, Ar), 168.27 (s, C-2), 190.0 (s, CO), 196.04 (s, CO) and 198.21 (s, CO).

2-*Amino*-3-*benzoyl*-1-p-*tolylpent*-2-*ene*-1,4-*dione* **3e**. This compound, obtained by treating benzoylacetone **1b** with *p*-toluoyl cyanide **2b** according to the method A, provided yellow crystals, m.p. 153–155 °C (58%) (Found: C, 74.5; H, 5.8; N, 4.4. $C_{19}H_{17}NO_3$ requires C, 74.2; H, 5.6; N, 4.6); ν_{max}(KBr)/cm^{-1} 3300, 1685, 1560 and 1260; δ_H($CDCl_3$) 1.93 (s, 3 H, Me), 2.35 (s, 3 H, Me), 6.6 (br, 1 H, NH), 7.14–7.59 (m, 9 H, Ar) and 10.7 (br, 1 H, NH); δ_C($CDCl_3$) 21.80 (q, *J* 127.2, Me), 30.85 (q, *J* 128.1, Me), 111.00 (s, C-3), 128.33 (d, *J* 146.4, Ar), 129.03 (d, *J ca.* 150, Ar), 129.19 (d, *J ca.* 150, Ar), 129.44 (d, *J ca.* 150, Ar), 131.70 (s, Ar), 132.41 (d, *J* 116.8, Ar), 140.41 (s, Ar), 145.42 (s, Ar), 164.26 (s, C-2), 191.34 (s, CO), 195.67 (s, CO) and 198.98 (s, CO).

2-*Amino*-3-*benzoyl*-4-*phenyl*-1-p-*tolylbut*-2-*ene*-1,4-*dione* **3f**. This compound, obtained by treating dibenzoylmethane **1c** with *p*-toluoyl cyanide **2b** according to the method A, afforded colourless crystals, m.p. 140–145 °C (36%) (Found: C, 78.3; H, 5.0; N, 3.5. $C_{24}H_{19}NO_3$ requires C, 78.0; H, 5.2; N, 3.8); ν_{max}(KBr)/cm^{-1} 3320, 1680 and 1570; δ_H($CDCl_3$) 2.36 (s, 3 H, Me), 6.2 (br, 1 H, NH), 6.99–7.41 (m, 10 H, Ar), 7.39 (d, *J* 8.2, 2 H, Ar), 7.84 (d, *J* 8.2, 2 H, Ar) and 10.3 (br, 1 H, NH); δ_C($CDCl_3$) 21.60 (q, *J* 125.9, Me), 109.68 (s, C-3), 127.66 (d, *J* 162.5, Ar), 127.83 (d, *J* 160.9, Ar), 128.95 (3 d, *J ca.* 161, Ar), 129.61 (d, *J* 159.7, Ar), 130.97 (s, Ar), 131.42 (d, *J* 161.1, Ar), 131.70 (d, *J* 159.7, Ar), 140.08 (s, Ar), 141.23 (s, Ar), 145.26 (s, Ar), 166.44 (s, C-2), 191.46 (s, CO), 194.63 (s, CO) and 196.33 (s, CO).

3-*Acetyl*-2-*amino*-1-p-*methoxyphenylpent*-2-*ene*-1,4-*dione* **3g**. This compound, obtained by treating acetylacetone **1a** with *p*-methoxybenzoyl cyanide **2c** according to the method A, formed colourless crystals, m.p. 161–165 °C (34%) (Found: C, 64.6; H, 5.8; N, 5.5. $C_{14}H_{15}NO_4$ requires C, 64.4; H, 5.8; N, 5.4); ν_{max}(KBr)/cm^{-1} 3340, 3200, 1670, 1640, 1580 and 1250; δ_H([$^2H_6$]DMSO) 2.27 (s, 3 H, Me), 2.45 (s, 3 H, Me), 3.84 (s, 3 H, OMe), 7.06 (d, *J* 8.4, 2 H, Ar), 7.70 (d, *J* 8.4, 2 H, Ar), 9.3 (br, 1 H, NH) and 10.8 (br, 1 H, NH); δ_C([$^2H_6$]DMSO) 30.55 (q, *J* 116.7, Me), 31.59 (q, *J* 126.7, Me), 55.36 (q, *J* 144.2, OMe), 111.06 (s, C-3), 113.79 (d, *J* 161.4, Ar), 127.69 (s, Ar), 130.07 (d, *J* 159.6 Ar), 162.85 (s, Ar), 168.05 (s, C-2), 188.09 (s, CO), 194.85 (s, CO) and 197.45 (s, CO).

2-*Amino*-3-*benzoyl*-1-p-*methoxyphenylpent*-2-*ene*-1,4-*dione* **3h**. This compound, obtained by treating benzoylacetone **1b** with *p*-methoxybenzoyl cyanide **2c** according to the method A, gave pale yellow crystals, m.p. 53–55 °C (88%) (Found: C, 70.4; H, 5.6; N, 4.2. $C_{19}H_{17}NO_4$ requires C, 70.6; H, 5.3; N, 4.3); ν_{max}(KBr)/cm^{-1} 3300, 3150, 1730, 1670, 1595, 1570 and 1250; δ_H($CDCl_3$) 1.97 (s, 3 H, Me), 3.77 (s, 3 H, OMe), 6.05 (br, 1 H, NH), 6.77 (d, *J* 8.8, 2 H, Ar), 7.20–7.47 (m, 5 H, Ar), 7.64 (d, *J* 8.8, 2 H, Ar) and 10.7 (br, 1 H, NH); δ_C($CDCl_3$) 21.02 (q, *J* 127.2, Me), 55.56 (q, *J* 143.9, OMe), 110.93 (s, C-3), 114.06 (d, *J* 161.1, Ar), 128.30 (d, *J* 159.9, Ar), 129.10 (d, *J* 141.2, Ar), 131.66 (d, *J* 172.7, Ar), 132.45 (d, *J* 152.6, Ar), 140.45 (s, Ar), 163.93 (s, C-2), 164.46 (s, Ar), 190.25 (s, CO), 195.88 (s, CO) and 198.91 (s, CO).

2-*Amino*-3-*benzoyl*-1-p-*methoxyphenyl*-4-*phenylbut*-2-*ene*-1,4-*dione* **3i**. This compound, obtained by treating dibenzoylmethane **1c** with *p*-methoxybenzoyl cyanide according to the method A, formed pale yellow crystals, m.p. 178–181 °C (50%) (Found: C, 74.6; H, 4.8; N, 3.8. $C_{24}H_{19}NO_4$ requires C, 74.8; H, 5.0; N, 3.6); ν_{max}(KBr)/cm^{-1} 3320, 3180, 1650, 1600 and 1570; δ_H($CDCl_3$) 3.82 (s, 3 H, Me), 6.4 (br, 1 H, NH), 6.88 (d, *J* 8.8, 2 H, Ar), 7.04–7.43 (m, 10 H, Ar), 7.91 (d, *J* 8.8, 2 H, Ar) and 10.35 (br, 1 H, NH); δ_C($CDCl_3$) 55.43 (q, *J* 144.8, OMe), 109.56 (s, C-3), 114.16 (d, Ar), 127.07 (d, Ar), 127.60 (d, Ar), 127.75 (d, Ar), 128.10 (d, Ar), 128.93 (d, Ar), 130.83 (d, Ar), 131.25 (d, Ar), 131.39 (s, Ar), 140.05 (s, Ar), 141.23 (s, Ar), 190.31 (s, CO), 194.64 (s, CO) and 196.20 (s, CO).

3-N-*Acetylamino*-4-*benzoyl*-5-*phenylpent*-3-*ene*-2,5-*dione* **4**. To a solution of dibenzoylmethane **1c** (0.897 g, 4 mmol) in 1,2-dichloromethane (4 cm^3) were added acetyl cyanide **2d** (0.34 cm^3, 4.8 mmol) and [Ni(acac)$_2$] (40 mg, 0.16 mmol). The reaction mixture was treated according to the method A to give compound **4** as a yellow oil (264 mg, 15%) (Found: C, 71.4; H, 5.2; N, 4.3. $C_{20}H_{17}NO_4$ requires C, 71.6; H, 5.1; N, 4.2); δ_H($CDCl_3$) 2.29 (s, 3 H, Me), 2.61 (s, 3 H, Me), 7.1–7.5 (m, 10 H, 2 Ph) and 11.93 (br, 1 H, NH); δ_C($CDCl_3$) 23.75 (Me), 31.13 (Me), 116.03 (C-4), 127.81 (Ph), 128.31 (Ph), 128.34 (Ph), 128.96 (Ph), 132.44 (Ph), 133.02 (Ph), 155.53 (C-3), 166.95 (CONH), 194.95 (CO), 196.62 (CO) and 197.44 (CO).

Methyl 2-*acetyl*-3-*amino*-4-*oxo*-4-*phenylbut*-2-*enoate* **8a**. This compound, obtained by treating methyl acetoacetate **6** with benzoyl cyanide **2a** according to the method B, afforded colourless crystals (75%), m.p. 134–135 °C (lit.,[7] m.p. 134–135 °C).

Methyl 2-*acetyl*-3-*amino*-4-*oxo*-4-p-*tolylbut*-2-*enoate* **8b**. This compound, obtained by treating methyl acetoacetate **6** with *p*-toluoyl cyanide **2b** according to method B, was a colourless oil (71.5%) (Found: C, 64.6; H, 5.5; N, 5.3.

$C_{14}H_{15}NO_4$ requires C, 64.4; H, 5.8; N, 5.4); ν_{max}(neat)/cm^{-1} 3340, 1730, 1680, 1630, 1450 and 1270; δ_H($CDCl_3$) 2.41 (s, 3 H, Me), 2.44 (s, 3 H, Me), 3.31 (s, 3 H, OMe), 6.6 (br, 1 H, NH), 7.25 (d, *J* 8.1, 2 H, Ar), 7.72 (d, *J* 8.1, 2 H, Ar) and 11.1 (br, 1 H, NH); δ_C($CDCl_3$) 21.82 (q, *J* 127.0, Me), 31.22 (q, *J* 128.5, Me), 50.80 (q, *J* 147.1, OMe), 100.42 (s, C-2), 128.76 (d, *J* 166.0, Ar), 129.65 (d, *J* 164.9, Ar), 131.51 (s, Ar), 145.22 (s, Ar), 166.54 (s, C-3), 168.94 (s, CO_2Me), 190.22 (s, CO) and 199.95 (s, CO).

A similar reaction carried out according to the method A failed to give compound **8b**.

Methyl 2-acetyl-3-amino-4-oxo-4-p-methoxyphenylbut-2-enoate **8c**. This compound, obtained by treating methyl acetoacetate **6** with *p*-methoxybenzoyl cyanide **2c** according to method B, was a yellow oil (66.6%). A similar reaction carried out according to method A gave compound **8c** in 25% yield (Found: C, 60.4; H, 5.2; N, 5.3. $C_{14}H_{15}NO_5$ requires C, 60.65; H, 5.45; N, 5.05); ν_{max}(neat)/cm^{-1} 3320, 1775, 1600 and 1300; δ_H($CDCl_3$) 2.42 (s, 3 H, Me), 3.32 (s, 3 H, OMe), 3.86 (s, 3 H, OMe), 6.8 (br, 1 H, NH), 6.91 (d, *J* 8.8, 2 H, Ar), 7.77 (d, *J* 8.8, 2 H, Ar) and 11.0 (br, 1 H, NH); δ_C($CDCl_3$) 31.17 (q, *J* 128.5, Me), 50.79 (q, *J* 145.1, OMe), 55.55 (q, *J* 146.3, OMe), 100.26 (s, C-2), 114.20 (d, *J* 162.1, Ar), 126.87 (s, Ar), 131.07 (d, *J* 164.4, Ar), 164.22 (s, Ar), 166.71 (s, CO_2Me), 167.31 (s, C-3), 189.31 (s, CO) and 199.87 (s, CO).

Methyl 3-amino-2-methoxycarbonyl-4-oxo-4-phenylbut-2-enoate **9a**. This compound, obtained by treating methyl malonate **7** with benzoyl cyanide **2a** according to the method B, provided colourless crystals, m.p. 119–121 °C (lit.,[7] m.p. 119–121 °C) (78%); ν_{max}(KBr)/cm^{-1} 3340br, 3220, 1690br, 1600, 1520, 1310 and 1260; δ_H($CDCl_3$) 3.28 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 6.30 (br, 1 H, NH), 7.44–7.58 (m, 3 H, Ph), 7.84 (d, *J* 7.0, 2 H, Ph) and 9.4 (br, 1 H, NH); δ_C($CDCl_3$) 51.17 (q, *J* 144.8, OMe), 51.62 (q, *J* 143.9, OMe), 91.27 (s, C-2), 128.54 (d, *J* 163.4, Ph), 128.86 (d, *J* 160.3, Ph), 134.01 (d, *J* 161.8, Ph), 134.01 (s, Ph), 165.50 (s, C-3), 165.88 (s, CO_2Me), 168.82 (s, CO_2Me) and 190.86 (s, C-4).

Methyl 4-amino-5-methoxy-5-phenyl-2-oxo-2,5-dihydrofuran-3-carboxylate **10a**. This compound, obtained by treating methyl malonate **7** with benzoyl cyanide **2a** according to method B and heating at reflux in ethyl acetate for 5 h, afforded colourless crystals, m.p. 188–190 °C (51.4%).

Conversion of **9a** *into* **10a**.—(a) A solution of compound **9a** (526 mg, 2 mmol) in ethyl acetate (10 cm^3) was treated with gaseous hydrochloric acid for 0.5 h, stirred at room temperature for 3 h and concentrated under reduced pressure: the resulting yellow oil was purified on a silica gel column (eluent: ethyl acetate–light petroleum, 1:1) to provide colourless crystals of **10a** (290 mg, 55.1%).

(b) A solution of **9a** (526 mg, 2 mmol) in ethyl acetate (10 cm^3) was treated with $SnCl_4$ (0.350 ml, 3 mmol). The reaction mixture was heated at 60 °C for 3 h and treated according to general procedure B: the resulting oil was purified on a silica gel column (eluent: ethyl acetate–light petroleum, 1:1) to provide colourless crystals of **10a** (310 mg, 58.9%) (Found: C, 59.4; H, 5.2; N, 5.1. $C_{13}H_{13}NO_5$ requires C, 59.3; H, 5.0; N, 5.3); ν_{max}(KBr)/cm^{-1} 3380, 3200br, 1740, 1660br, 1590, 1460, 1310 and 1260; δ_H([$^2H_6$]DMSO) 3.29 (s, 3 H, OMe), 3.69 (s, 3 H, OMe), 7.41–7.52 (m, 5 H, Ph), 8.42 (s, 1 H, NH) and 8.79 (s, 1 H, NH); δ_C([$^2H_6$]DMSO) 50.57 (q, *J* 143.5, OMe), 50.82 (q, *J* 146.1, OMe), 85.31 (s, C-5), 102.26 (s, C-3), 125.63 (d, *J* 160.6, Ph), 128.46 (d, *J* 160.2, Ph), 129.52 (d, *J* 158.8, Ph), 136.46 (s, Ph), 163.13 (s, CO_2Me), 166.01 (s, C-4) and 171.55 (s, C-2).

Methyl 4-amino-5-methoxy-5-methyl-2-oxo-2,5-dihydrofuran-3-carboxylate **10b**. This compound, obtained by treating methyl malonate **7** with acetyl cyanide **2d** according to method B in benzene and heating at reflux for 3 h (yield 82%), or in ethyl acetate with stirring of the reaction mixture at room temperature for 24 h (yield 46%), gave yellow crystals, m.p. 205–210 °C (Found: C, 47.6; H, 5.3; N, 7.1. $C_8H_{11}NO_5$ requires C, 47.8; H, 5.5; N, 7.0); ν_{max}(KBr)/cm^{-1} 3480, 3260, 3200, 1740, 1650 and 1320; δ_H([$^2H_6$]DMSO) 1.57 (s, 3 H, Me), 3.06 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 8.40 (s, 1 H, NH) and 8.93 (s, 1 H, NH); δ_C([$^2H_6$]DMSO) 23.05 (q, *J* 129.6, Me), 50.08 (q, *J* 143.8, OMe), 50.46 (q, *J* 146.9, OMe), 85.23 (s, C-5), 101.65 (s, C-3), 163.27 (s, CO_2Me), 165.67 (s, C-4) and 171.82 (s, C-2).

X-Ray Analysis. Colourless crystals of $C_8H_{11}NO_5$, suitable for X-ray analysis (0.4 × 0.4 × 0.6 mm) were obtained by recrystallisation of the crude derivative from acetone. They are triclinic, space group $P\bar{1}$, with a = 9.516(1), b = 7.245(1), c = 6.915(1) Å, α = 94.4(1), β = 98.4(1), γ = 81.2(1)°; Z = 2; D = 1.44 g cm^{-3}. Crystal data were obtained from a single-crystal diffractometric measurement; 2253 unique reflections up to θ = 28° were collected on a Philips PW 1100 four-cycle diffractometer operating in the θ–2θ scan mode, using a Mo-Kα monochromatized radiation (λ 0.7107 Å). The positional parameters of the non-hydrogen atoms were determined by direct methods using the SHELXS 86 phasing program.[17] After a few cycles of full-matrix least-squares refinement (using anisotropic thermal parameters), all the H atoms were located in a difference Fourier map and enclosed in the last refinement with isotropic thermal parameters. The final R value for 1878 reflections with $F > 6\sigma(F)$ was R = 0.045 [R_w = 0.056, w = $1/(\sigma^2(F) + 0.00772F^2)$]. Fractional coordinates together with anisotropic thermal parameters for non-hydrogen atoms, and fractional coordinates of H-atoms have been deposited with the Cambridge Data Centre.*

3-Acetyl-4-amino-1-benzyl-5-hydroxy-5-phenylpyrrol-2(5H)-one **13a**. This compound, obtained by treating *N*-acetoacetylbenzylamide **11a** with benzoyl cyanide **2a** according to the method B, provided brown crystals (90%), m.p. 225–227 °C (lit.,[7] m.p. 230–232 °C); ν_{max}(KBr)/cm^{-1} 3350, 3200, 1640 and 1520; δ_H([$^2H_6$]DMSO) 2.39 (s, 3 H, Me), 3.86 (d, *J* 15.6, 1 H, CH_2), 4.31 (d, *J* 15.6, 1 H, CH_2), 7.14–7.36 (m, 10 H, Ar), 7.20 (s, 1 H, OH), 8.37 (br, 1 H, NH), 8.74 (br, 1 H, NH); the signals 7.20, 8.37 and 8.74 exchange with D_2O in *ca.* 3 min; δ_C([$^2H_6$]DMSO) 27.49 (q, *J* 126.3, Me), 69.73 (t, *J* 138.2, CH_2), 87.53 s, C-5), 97.32 (s, C-3), 126.07 (d, *J* 157.3, Ar), 126.17 (d, *J* 157.3, Ar), 127.62 (two d, *J ca.* 150, Ar), 128.24 (d, *J* 160.7, Ar), 128.38 (d, *J* 160.7, Ar), 138.23 (s, Ar), 139.11 (s, Ar), 168.73 (s, C-4), 173.48 (s, C-2) and 193.81 (s, CO).

3-Acetyl-4-amino-1-benzyl-5-hydroxy-5-p-tolylpyrrol-2(5H)-one **13b**. This compound, obtained by treating *N*-acetoacetylbenzylamide **11a** with *p*-toluoyl cyanide **2b** according to the method B, afforded brown crystals (90%), m.p. 215–220 °C (Found: C, 71.2; H, 6.2; N, 8.1. $C_{20}H_{20}N_2O_3$ requires C, 71.4; H, 6.0; N, 8.3); ν_{max}(KBr)/cm^{-1} 3360, 3200, 1640, 1525 and 1430; δ_H([$^2H_6$]DMSO) 2.27 (s, 3 H, Me), 2.37 (s, 3 H, Me), 3.80 (d, 1 H, *J* 15.6, CH_2), 4.32 (d, 1 H, *J* 15.6, CH_2), 7.12–7.25 (m, 10 H, Ar and OH), 8.33 (br, 1 H, NH) and 8.71 (br, 1 H, NH).

A similar reaction carried out according to the method A failed to give compound **13b**.

3-Acetyl-4-amino-1-benzyl-5-hydroxy-5-p-methoxyphenylpyrrol-2(5H)-one **13c**. This compound, obtained by treating *N*-acetoacetylbenzylamide **11a** with *p*-methoxybenzoyl cyanide **2c** according to the method B, afforded brown crystals (90%), m.p. 232–235 °C (Found: C, 68.1; H, 5.6; N, 8.1. $C_{20}H_{20}N_2O_4$ requires C, 68.2; H, 5.7; N, 7.95); ν_{max}(KBr)/cm^{-1} 3360, 3240, 1640 and 1510; δ_H([$^2H_6$]DMSO) 2.38 (s, 3 H, Me), 3.73 (s, 3 H, OMe), 3.84 (d, *J* 15.7, 1 H, CH_2), 4.31 (d, *J* 15.7, 1 H, CH_2), 6.88 (d, *J* 8.7, 2 H, Ar), 7.11 (s, 1 H, OH), 7.16 (s, 5 H, Ar), 7.25 (d, *J* 8.7, 2 H, Ar), 8.32 (br, 1 H, NH) and 8.71 (br, 1 H, NH);

* For details of the scheme see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

$\delta_C([^2H_6]DMSO)$ 27.47 (q, *J* 126.4, Me), 55.05 (q, *J* 143.4, OMe), 69.7 (t, *J* 139.6, CH_2), 87.49 (s, C-5), 97.18 (s, C-3), 113.58 (d, *J* 161.3, Ar), 126.15 (d, *J* 158.9, Ar), 127.46 (d, *J* 157.8, Ar), 127.61 (two d, *J* 157.8, Ar), 130.03 (s, Ar), 139.03 (s, Ar), 159.26 (s, Ar), 168.67 (s, C-4), 173.69 (s, C-2) and 193.80 (s, CO).

When the same reaction was carried out according to the method A the compound **13c** was obtained in 25% yield.

3-*Acetyl*-4-*amino*-5-*hydroxy*-1,5-*diphenylpyrrol*-2(5H)-*one* **13d**. This compound, obtained by treating *N*-acetoacetanilide **11b** with benzoyl cyanide **2a** according to the method B formed brown crystals (62%), m.p. 228–231 °C (Found: C, 70.4; H, 5.3; N, 9.0. $C_{18}H_{16}N_2O_3$ requires C, 70.1; H, 5.2; N, 9.1); ν_{max}(KBr)/cm^{-1} 3380, 3240, 1700, 1650 and 1540; $\delta_H(CDCl_3)$ 2.42 (s, 3 H, Me), 6.14 (br, 1 H, NH), 6.15 (br, 1 H, OH), 6.95–7.47 (m, 10 H, Ar) and 8.66 (br, 1 H, NH); $\delta_C([^2H_6]DMSO)$ 27.87 (q, *J* 127.3, Me), 88.35 (s, C-5), 97.11 (s, C-3), 124.36 (d, *J* 153.1, Ar), 124.67 (d, *J* 156.5, Ar), 126.04 (d, *J* 160.5, Ar), 127.94 (d, *J* 160.6, Ar), 128.24 (d, *J* 160.9, Ar), 136.77 (s, Ar), 138.16 (s, Ar), 167.96 (s, C-4), 173.22 (s, C-2) and 194.27 (s, CO).

When the reaction was carried out according to the method A compound **13d** was obtained in 30.7% yield.

3-*Acetyl*-4-*amino*-5-*hydroxy*-1-*phenyl*-5-p-*tolylpyrrol*-2(5H)-*one* **13e**. This compound, obtained by treating *N*-acetoacetanilide **11b** with *p*-toluoyl cyanide **2b** according to the method B afforded brown crystals (82%), m.p. 108–115 °C (Found: C, 70.6; H, 5.5; N, 8.8. $C_{19}H_{18}N_2O_3$ requires C, 70.8; H, 5.6; N, 8.7); ν_{max}(KBr)/cm^{-1} 3260br, 1660, 1500 and 1360; $\delta_H([^2H_6]DMSO)$ 2.23 (s, 3 H, Me), 2.46 (s, 3 H, Me), 6.99–7.46 (m, 9 H, Ar), 7.71 (s, OH), 8.37 (br, 1 H, NH) and 8.80 (br, 1 H, NH).

A similar reaction when carried out according to method A failed to give compound **13e**.

3-*Acetyl*-4-*amino*-5-*hydroxy*-5-p-*methoxyphenyl*-1-*phenylpyrrol*-2(5H)-*one* **13f**. This compound, obtained by treating *N*-acetoacetanilide **11b** with *p*-methoxybenzoyl cyanide **2c** according to the method B formed brown crystals (95%), m.p. 100–105 °C.

A similar reaction carried out according to method A gave a complex reaction mixture containing little (5%) of compound **13f** (Found: C, 67.4; H, 5.2; N, 8.1. $C_{19}H_{18}N_2O_4$ requires C, 67.4; H, 5.4; N, 8.3); ν_{max}(KBr)/cm^{-1} 3380, 3230, 1680, 1635 and 1510; $\delta_H(CDCl_3)$ 2.43 (s, 3 H, Me), 3.70 (s, 3 H, OMe), 5.79 (br, 1 H, NH), 6.02 (br, 1 H, OH), 6.73 (d, *J* 8.7, 2 H, Ar), 6.9–7.07 (m, 3 H, Ar), 7.22–7.28 (m, 4 H, Ar) and 8.66 (br, 1 H, NH); $\delta_C([^2H_6]DMSO)$ 27.85 (q, *J* 126.5, Me), 54.96 (q, *J* 143.3, OMe), 88.26 (s, C-5), 96.96 (s, C-3), 113.55 (d, *J* 162.9, Ar), 124.28 (d, *J* 162.3, Ar), 124.63 (d, *J* 159.4, Ar), 127.42 (d, *J* 155.8, Ar), 127.93 (d, *J* 160.0, Ar), 129.96 (s, Ar), 136.85 (s, Ar), 159.06 (s, Ar), 167.88 (s, C-4), 173.41 (s, C-2) and 194.24 (s, CO).

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