309 mg (61% based on 3) of **16c**. Compound **16c** was characterized by comparison (TLC, ^{1}H NMR, IR, and mass spectra) with an authentic sample prepared from the Wittig–Horner reagent 2.[4]

2-[4-(2,6-Diphenyl-4*H*-pyranylidenyl)]propanaldehyde (15e). A solution of the Wittig–Horner reagent 1[2] was prepared by dropwise addition of 2.85 mL (1 equiv) of *n*-BuLi (2.1 M in hexane) to a stirred solution of 2.0 g (0.0058 mol) of diethyl (2,6-diphenyl-4*H*-pyran-4-yl)phosphonate[2] in 50 mL of THF at −77 °C. The dark green anion solution was stirred for 5 min at −77 °C and then added slowly (over 5 min) through a transfer needle with positive argon pressure into a stirred solution of 1.4 mL (2 equiv) of distilled pyruvaldehyde dimethyl acetal in 10 mL of THF at −77 °C. The reaction mixture was allowed to equilibrate to room temperature and stirred for 1 h. Acetic acid (2 mL) was added slowly. The mixture was stirred for 15 min and poured into a stirred two-phase mixture of 200 mL of saturated Na_2CO_3 and 200 mL of ether. Water (100 mL) was added, the mixture was partitioned, separated, dried over $MgSO_4$, and filtered, and the solvent was removed on a rotary evaporator. The residue was recrystallized from 30 mL of cyclohexane to yield 580 mg (35%) of **15e**: mp 194–195.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 3, Me), 6.78 (d, 1, J = 2 Hz), 7.60 (d, 1, J = 2 Hz), 7.43 (m, 6), 7.75 (m, 4), 10.10 (s, 1); mass spectrum, m/e 288 (M^+ for $C_{20}H_{16}O_2$).

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.3; H, 5.6. Found: C, 82.8; H, 5.7.

1-[4-(2,6-Diphenyl-4*H*-thiopyranylidenyl)]-1-phenylethane (16f). A solution of the Wittig–Horner reagent 2[3] was prepared from 6.5 g (0.0186 mol) of thiopyrylium perchlorate 9[11] in 60 mL of THF and 11 mL (1.2 equiv) of a solution of diethyl sodium phosphonate in benzene (1.9 M) at −77 °C followed by 1.2 equiv of *n*-BuLi under argon (2.4 M in hexanes). A solution of 2.68 g (0.022 mL) of acetophenone in 10 mL of THF was added, and the reaction mixture was allowed to equilibrate to room temperature in 4 h. The reddish brown mixture was poured into a beaker containing 500 mL of water. The precipitated gum was removed from the water by decantation and then stirred in ether. The insoluble solid was collected by filtration and recrystallized from 100 mL of acetonitrile to give 1 g (15%) of pure **16f**: mp 166–167 °C; ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 3, Me), 6.75 (s, 1), 6.86 (s, 1), 7.15–7.64 (m, 15, Ar H); mass spectrum, m/e 352 (M^+).

Anal. Calcd for $C_{25}H_{20}S$: C, 85.2; H, 5.7. Found: C, 84.8; H, 5.7.

Registry No. **1**, 75548-91-3; **2**, 75548-92-4; **3**, 80160-61-8; **5**, 55221-37-9; **6**, 71750-06-6; **7**, 80160-62-9; **9**, 13586-29-3; **10**, 57094-07-2; **11**, 80160-63-0; **12**, 80160-64-1; **13**, 80160-65-2; **14**, 80160-66-3; **15a**, 100-10-7; **15b**, 492-22-8; **15c**, 20399-89-7; **15d**, 75548-93-5; **15e**, 40564-75-8; **15f**, 98-86-2; **16a**, 73453-38-0; **16b**, 73453-37-9; **16c**, 75548-95-7; **16d**, 51829-03-9; **16e**, 80160-67-4; **16f**, 80160-68-5; **17**, 6342-56-9.

Effect of Metal Ions in Organic Synthesis. Part 10. Synthesis and X-ray Crystal Structure of Some 1-(Arylamino)pyrrole Derivatives by Reaction of (Arylazo)alkenes and β-Dicarbonyl Compounds in the Presence of Copper(II) Chloride

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A mild, simple, and convenient method for the synthesis of some 1-(arylamino)pyrrole derivatives by reaction of (arylazo)alkenes and β-dicarbonyl compounds is reported. This reactivity appears to be catalyzed by copper(II) chloride dihydrate, takes place in very mild conditions, does not require a strong acid or base, seems to be successfully applicable to different (arylazo)alkenes and β-dicarbonyl derivatives, and frequently provides good yields. In particular, the reaction products of [(*p*-nitrophenyl)azo]cyclohexene and (phenylazo)stilbene with ethyl acetoacetate were examined. The X-ray diffraction study unambiguously demonstrated that the molecular structures of these compounds contain a pyrrole ring instead of a dihydropyridazine ring, as previously reported for analogous products. The details of the molecular parameters are presented and discussed.

In our previous papers some effects of metal ions in certain organic synthesis have been presented.[1] In particular, we reported the stereospecific 1,4 addition reactions of certain alcohols, water, and phenol to the azo-ene system of (phenylazo)stilbene in the presence of copper and iron ions. The role of the metal ions in these reactivities was also discussed.[2]

In continuation of these investigations, the reaction of some (arylazo)alkenes (**1a–c**) and β-dicarbonyl compounds (**2**) in the presence of copper(II) chloride dihydrate (M) has been studied.[3] While in the absence of this inorganic salt no reaction was observed, in the presence of copper(II) ions the above-mentioned reaction easily occurs, providing the 1-(arylamino)pyrrole derivatives (**4a–e**), as shown in Table I. The molecular ratio between the (arylazo)alkene derivative and copper(II) chloride (1:M), the reaction times and procedures, the yields and melting points of the reaction products are also listed in Table I.

In accordance with previous findings on this matter, the reaction probably occurs by 1,4 addition of the β-dicarbonyl compounds to the azo-ene system of the (arylazo)alkene derivatives (**3**), followed by ring closure and elimination to give the pyrrole ring (**4a–e**).[2-5] Since the

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[1] O. Attanasi and S. Gasperoni, *Gazz. Chim. Ital.* **108**, 137 (1978); O. Attanasi, S. Gasperoni, and C. Carletti, *Chim. Ind.* (*Milan*), **60**, 654 (1978); *J. Prakt. Chem.*, **322**, 1063 (1980); O. Attanasi and F. Serra-Zanetti, *Synthesis*, 314 (1980); *Org. Prep. Proced. Int.*, **13**, 170 (1981), and references therein.

[2] O. Attanasi, *Stud. Urbinati, Fac. Farm.*, **17**, 123 (1975); O. Attanasi, P. Battistoni, and G. Fava, *Synth. Commun.*, **9**, 465 (1979); *J. Org. Chem.*, **46**, 447 (1981), and references therein.

[3] O. Attanasi and P. Bonifazi, 12th Convegno Nazionale Chimica Organica, Società Chimica Italiana, Ancona, Sept 14–19, 1980 p 131.

[4] L. Bernardi, P. Masi, and G. Rosini, *Ann. Chim.* (*Rome*), **63**, 601 (1973).

[5] S. Brodka and H. Simon, *Justus Liebigs Ann. Chem.*, **745**, 193 (1971).

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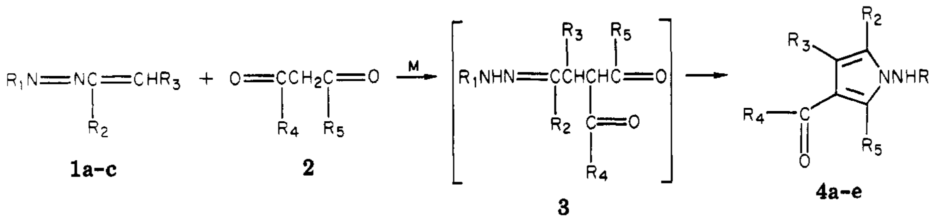
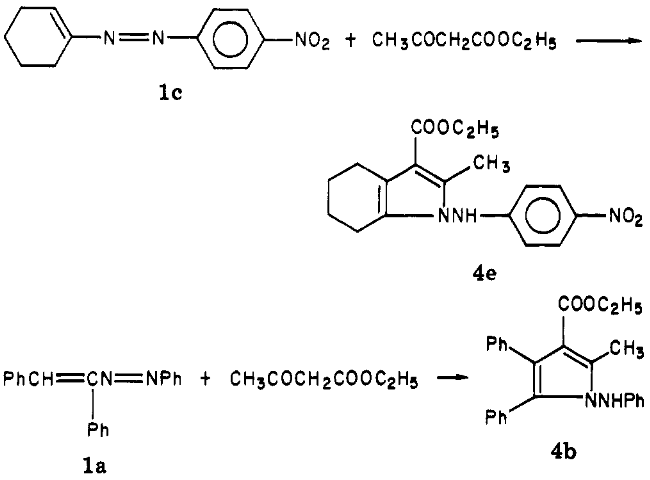
Table I. Molecular Ratio between the (Arylazo)alkene Derivatives and Copper(II) Chloride Dihydrate (1:M), Reaction Procedures and Times, Yields, and Melting Points of the Reaction Products



(arylazo)alkenes				pyrroles							
no.	R_1	R_2	R_3	no.	R_4	R_5	1:M	procedure[a]	mp,[b] °C	t, h	% yields
1a	C_6H_5	C_6H_5	C_6H_5	4a	CH_3	CH_3	8:1	A	145-146	1	85
				4b	C_2H_5O	CH_3	8:1	B	161-162	1.5	75
				4c	$-(CH_2)_3-$		1:1	C	212-213	24	40
1b	C_6H_5	$C_6H_5CH_2$	C_6H_5	4d	CH_3	CH_3	8:1	A	160-162	3	75
1c	p-$NO_2C_6H_4$	$-(CH_2)_4-$		4e	C_2H_5O	CH_3	8:1	B	153-154	2.5	40

[a] See Experimental Section. [b] Melting points are uncorrected.

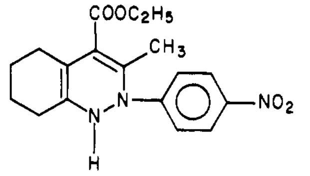
Scheme I



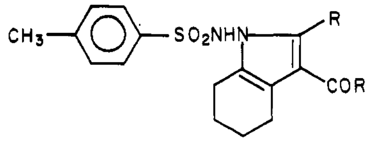
amount of copper(II) chloride dihydrate was in several cases much less than the stoichiometric (see Table I and Experimental Section), a catalytic role for the copper(II) ions can be hypothesized. Very likely, organometallic complexes between (arylazo)alkenes and metal ions promote the azo-ene system activation with respect to the 1,4 addition of the β-dicarbonyl compounds. It is well-known that several of these latter form complexes and chelates with metal ions, and particularly with copper(II) ions. The easy reaction observed can be ascribed to the higher reactivity between the reagents as organometallic complexes than that between the pure reagents. After the reaction the metal ions would regenerate in the original form and would become again operative until the reaction was complete. These hypotheses are also supported by our previous investigations.[1,2]

The reactions take place under very mild conditions (magnetic stirring at room temperature) without strong acid or base, appear to be successfully applicable to different (arylazo)alkenes and β-dicarbonyl derivatives, and frequently provide good yields. The 1-(arylamino)pyrrole derivatives are not easily synthesized by other known methods.[7] For these reasons, the procedure reported here represents a mild, simple, and convenient method for the synthesis of the above-mentioned compounds.

However, in the assignment of structures to the reaction products **4a–e**, many uncertainties were immediately apparent. In fact, Brodka and Simon have reported the formation of 1,2,5,6,7,8-hexahydro-3-methyl-2-(p-nitrophenyl)-4-(ethoxycarbonyl)cinnoline (**5**) by addition of ethyl acetoacetate to [(p-nitrophenyl)azo]cyclohexene,[5] while Bernardi et al. have obtained tetrahydroindole derivatives (**6**) from analogous reactions of (tosylazo)cyclohexene with β-dicarbonyl compounds.[4]



5



6

On the other hand, the mass spectra of the reaction products obtained in our investigations showed the loss of ArNH (see Experimental Section), in good agreement with the loss of TsNH observed by Bernardi et al. for the tosylamino derivatives of tetrahydroindole compounds (**6**).[4] In some cases, specifically discussed below, the mass spectra of these derivatives exhibited the peaks related to the loss of ArNH as the base peak (100%). However, since the usual spectroscopic and physicochemical techniques (UV, IR, ^1H and ^{13}C NMR, MS, elemental analysis, etc.) did not permit an unambiguous assignment, an X-ray diffraction study was carried out to define the structures.

Initially the reaction of [(p-nitrophenyl)azo]cyclohexene (**1c**) and ethyl acetoacetate was considered. The product **4e** synthesized according to the procedure of Brodka et al.[5] exhibited identical spectroscopic, physicochemical, and crystal properties with that obtained by our procedure and showed unequivocally to be a tetrahydroindole derivative, in accordance with the assignment by Bernardi et al.[4] and in disagreement with the assignment by Brodka et al.[5] However, the decomposition of this product from the X radiation hindered a good refinement of the structure, giving an R value of 30% (see Experimental Section). This fact did not allow a complete determination of the mo-

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(6) B. F. Bonini, G. Maccagnani, G. Mazzanti, G. Rosini, and E. Foresti, *J. Chem. Soc., Perkin Trans. 1*, 2322 (1981), and references therein.

(7) H. H. Inhoffen, J. W. Buchler, and P. Jager, *Forschr. Chem. Org. Naturst.*, **26**, 284 (1968); A. Gossauer, "Die Chemie der Pyrrole", Springer-Verlag, New York, 1974.

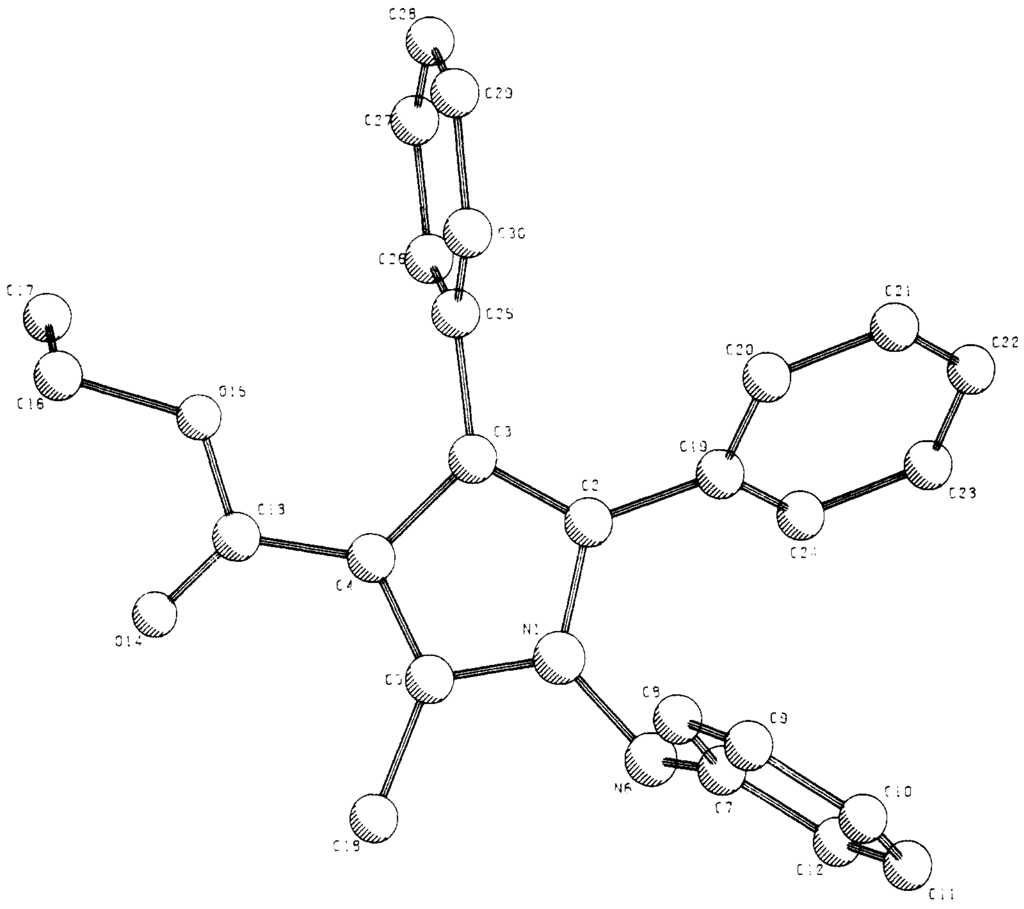

Figure 1. The molecule **4b** viewed normally to the plane formed by N(1), C(3), and C(4), showing the atom numbering system used in the crystallographic analysis.

lecular parameters. Notwithstanding, the *E* map revealed all the nonhydrogen atoms.

For these reasons and in order to obtain a complete elucidation of the molecular structure, we examined the reaction of (phenylazo)stilbene (**1a**) with ethyl acetoacetate. The product **4b** obtained in accordance with the method of Brodka et al.[5] exhibited once again identical spectroscopic, physicochemical, and crystal properties with that prepared by our method. The molecular structure of **4b** is shown in Figure 1 and the crystal packing of **4b** is given in Figure 2 (available as supplementary material).

In this case it was possible to obtain a good refinement of the structure with an *R* value of 8.8% (see Experimental Section). Complete data for the crystallography are listed in Tables 1–8 (see paragraph at the end of paper about supplementary material). The sum of the bond angles around the nitrogen heteroatom is close to 360°, showing this atom to be sp^2 hybridized. Furthermore, these data indicate that the five-membered aromatic heterocycle is a nearly regular and perfectly planar pentagon containing very similar bond lengths and angles. In fact, only the bond angle C(2)–N(1)–C(5) is significantly larger (by 3°) than the 108° value. Indeed, the sum of the bond angles involving the atoms of this ring is exactly 540°. For these reasons, the deviations from the plane for the atoms of the heterocycle ring are very small. These data are in good agreement with the findings of Bonnett et al.[8]

The plane of the two phenyl groups at C(3) and N(6) are nearly orthogonal with that of the pyrrole ring, while the plane of the phenyl group at C(2) forms an angle of 126° with that of the same ring. Furthermore, the phenyl group at N(6) is completely above the plane of the five-membered aromatic heterocycle, while the other two phenyl groups are partially above and partially under the same plane. The geometries of the phenyl, methyl, and carbethoxy groups are almost normal.

In conclusion, it seems unequivocally demonstrated that these reactions follow the behavior shown in Scheme I.

Further investigations are in progress in our laboratories to extend and generalize these and related reactions and elucidate the kinetic and mechanistic aspects.

Experimental Section

(Arylazo)alkenes 1a–c. These compounds were synthesized as previously reported.[2,5,6]

β-Dicarbonyl Derivatives 2. These compounds were commercial materials and were used without further purification.

Reaction of (Arylazo)alkenes and β-Dicarbonyl Compounds. Procedure A for the Synthesis of Compounds 4a and 4b. Copper(II) chloride dihydrate (0.22 and 0.21 mmol, respectively) dissolved in 2,4-pentanedione (7 mL) was added to a solution of (arylazo)alkene (1.76 mmol of (phenylazo)stilbene **1a** or 1.68 mmol of (phenylazo)diphenylpropene **1b**, respectively) in 2,4-pentanedione (7 mL). The mixture was stirred magnetically at room temperature during 1 or 3 h, respectively, until the reaction was completed (monitored by silica gel TLC). After evaporation of 2,4-pentanedione under reduced pressure, the crude reaction product was poured into methylene chloride and washed several times with water. The organic layer was dried with anhydrous sodium sulfate, and after evaporation under reduced pressure, it provided the relative 1-(phenylamino)pyrrole derivatives **4a** and **4d**.

Procedure B for the Synthesis of Compounds 4b and 4e. Copper(II) chloride dihydrate (0.22 and 0.27 mmol, respectively) dissolved in tetrahydrofuran (15 mL) was added to a solution of

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[8] R. Bonnett, M. B. Hursthouse, and S. Neidle, *J. Chem. Soc, Perkin Trans. 2*, 902 (1972).

(arylazo)alkene (1.76 mmol of (phenylazo)stilbene **1a** or 2.16 mmol of [(*p*-nitrophenyl)azo]cyclohexene **1c**, respectively) in ethyl acetoacetate (15 mL). The mixture was stirred magnetically at room temperature during 1.5 or 2.5 h, respectively, until the reaction was completed (monitored by silica gel TLC). Afterward the reaction was treated as described above in detail, providing the relative 1-(arylamino)pyrrole derivatives **4b** and **4e**.

Procedure C for the Synthesis of Compound 4c. 1,3-Cyclohexanedione (17.6 mmol) dissolved in tetrahydrofuran (10 mL) was added to a solution of (phenylazo)stilbene **1a** (1.76 mmol) in tetrahydrofuran (10 mL) and then copper(II) chloride dihydrate (1.76 mmol) dissolved in tetrahydrofuran (20 mL) was added. The mixture was stirred magnetically at room temperature during 24 h, until the reaction was completed (monitored by silica gel TLC). Afterward the reaction was treated as described above in detail, providing the relative 1-(phenylamino)pyrrole derivative **4c**.

Purification of Compounds 4a–e. In general the crude reaction products **4a–e** were purified by crystallization with methylene chloride–petroleum ether (40–60 °C; or *n*-hexane). In the particular case of the products **4c** and **4e** a preliminary purification by chromatography on a silica gel column may be necessary (at first elution with cyclohexane and then with cyclohexane–ethyl acetate mixtures, gradually increasing the amount of ethyl acetate to a 90/10 (v/v) ratio).

Analytical Data of Compounds 4a–e. Compound 4a: yields 85%; mp 145–146 °C (uncorrected); crystallized by methylene chloride–*n*-hexane; IR (Nujol) 3240 (NH), 1640 (>C=O), 1600 cm^{-1} (aromatic); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.95 (3 H, s), 2.45 (3 H, s), 6.35–7.35 (16 H, m; at 6.8, 1 H, s, D$_2$O exchange); mass spectrum, *m/e* 367 (17, M$^+$ + 1), 366 (58, M$^+$), 351 (6), 324 (9), 323 (10), 275 (23), 274 (100, M – PhNH), 259 (5), 258 (5), 231 (6), 230, (17), 189 (6), 128 (6), 127 (5). Anal. Calcd for $C_{25}H_{22}N_2O$: C, 81.94; H, 6.05; N, 7.64. Found: C, 81.61; H, 6.14; N, 7.64.

Compound 4b: yields 75%; mp 153–154 °C (uncorrected); crystallized by methylene chloride–petroleum ether (40–60 °C); IR (Nujol) 3240 (NH), 1665 (COO), 1600 (aromatic), 1505, 1330 cm^{-1} (NO$_2$); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.4 (3 H, t, J = 7 Hz), 1.6–3 (11 H, m; s at 2.4), 4.3 (2 H, q, J = 7 Hz), 6.5 (2 H, d, J = 9 Hz), 8.1 (2 H, d, J = 9 Hz), 7.9 (1 H, s, D$_2$O exchange); mass spectrum, *m/e* 344 (22, M$^+$ + 1), 343 (100, M$^+$), 328 (10), 315 (12), 314 (52), 298 (15), 282 (10), 270 (28), 207 (10), 206 (25, M – *p*-(NO$_2$Ar)NH), 205 (10), 178 (35), 177 (10), 162 (10), 161 (10), 160 (26), 158 (14), 149 (15), 134 (36), 133 (20), 132 (32), 130 (13), 117 (13), 91 (17). Anal. Calcd for $C_{18}H_{21}N_3O_4$: C, 62.95; H, 6.16; N, 12.24. Found: C, 63.12; H, 6.22; N, 12.66.

Compound 4c: yields 40%; mp 212–213 °C (uncorrected); crystallized by methylene chloride–petroleum ether (40–60 °C); IR (Nujol) 3230 (NH), 1640 (>C=O), 1600 cm^{-1} (aromatic); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.95–2.95 (6 H, m), 6.35–7.45 (16 H, m; at 6.65, 1 H, s, D$_2$O exchange); mass spectrum, *m/e* 379 (39, M$^+$ + 1), 378 (84, M$^+$), 323 (12), 301 (10), 287 (44), 286 (100, M – PhNH), 274 (10), 258 (17), 244 (17), 230 (25), 127 (26), 93 (22). Anal. Calcd for $C_{26}H_{22}N_2O$: C, 82.51; H, 5.86; N, 7.40. Found: C, 82.46; H, 5.88; N, 7.26.

Compound 4d: yields 75%; mp 160–162 °C (uncorrected); crystallized by methylene chloride–petroleum ether (40–60 °C); IR (Nujol) 3220 (NH), 1630 (>C=O), 1600 cm^{-1} (aromatic); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.95 (3 H, s), 2.45 (3 H, s), 7.60 (2 H, s), 6.1 (1 H, s, D$_2$O exchange), 6.3–7.4 (15 H, m); mass spectrum, *m/e* 381 (54, M$^+$ + 1), 380 (100, M$^+$), 365 (16), 338 (24), 337 (24), 289 (54), 288 (92, M – PhNH), 274 (19), 246 (81), 244 (43), 230 (19), 220 (14), 202 (14), 168 (16), 128 (19), 127 (18), 115 (22), 106 (16), 103 (15), 93 (57), 91 (43). Anal. Calcd for $C_{26}H_{24}N_2O$: C, 78.76; H, 6.10; N, 7.07. Found: C, 78.87; H, 6.13; N, 6.95.

Compound 4e: yields 40%; mp 161–162 °C (uncorrected); crystallized by methylene chloride–*n*-hexane; IR (Nujol) 3300 (NH), 1665 (COO), 1600 cm^{-1} (aromatic); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1 (3 H, t, J = 7 Hz), 2.5 (3 H, s), 4 (2 H, q, J = 7 Hz), 6.3–7.3 (16 H, m; at 6.6, 1 H, s, D$_2$O exchange); mass spectrum, *m/e* 397 (18, M$^+$ + 1), 396 (58, M$^+$), 381 (7), 367 (7), 351 (4), 323 (8), 305 (5), 304 (20, M – PhNH), 277 (5), 276 (21), 260 (4), 259 (24), 258 (100), 230 (10), 220 (4), 189 (4), 128 (7), 127 (16), 93 (8), 92 (5). Anal. Calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07. Found: C, 79.67; H, 6.13; N, 6.95.

X-ray Analysis of Compounds 4b and 4e. Precise unit-cell dimensions were determined by a least-squares fit on 23 independent 2θ values. Intensity data were collected by a PW 1100 Philips four-circle diffractometer using $\omega/2\theta$ scan; θ range, 2° ≤ θ ≤ 25°; scan speed, 0.04° s^{-1}; scan width, 1.20°; counting background, 20 s on either side of the peak; MoK α radiation, λ = 0.7107 Å; graphite monochromator.

Crystal Data of Compound 4e: approximate sample dimensions, 0.76 × 0.28 × 1.20 mm; $C_{18}H_{21}N_3O_4$; mol. wt. 343.37; monoclinic; space group $P2_1/a$; a = 17.08 Å, b = 8.34 Å, c = 12.40 Å, β = 101.33°, V = 1731.5 Å^3, D_c = 1.32 g cm^{-3}, Z = 4; $\mu_{(\mathrm{MoK}\alpha)}$ = 0.57 cm^{-1}; $F(000)$ = 728.00; number of reflections measured, 2721; number of unique reflections, 2401.

Structure Determination and Refinement. The structure was solved by direct methods, using the crystallographic program system SHELX (Sheldrick, 1976).[9] The E map indicated the position for all the nonhydrogen atoms. However, because of the product decomposition from the X radiations, the refinement, using 1357 reflections with $F_o > 2.0\sigma(F_o)$, gave an R value of 0.30. Drawings were made with PLUTO (Motherwell, 1976).[10]

Crystal Data of Compound 4b: approximate sample dimensions, 0.35 × 0.45 × 0.55 mm; $C_{26}H_{24}N_2O_2$; mol wt 396.82; triclinic; space group $P\bar{1}$; a = 12.152 Å, b = 10.724 Å, c = 8.728 Å, α = 104.90°, β = 99.92°, γ = 88.09°, V = 1082.65 Å^3, D_c = 1.21 g cm^{-3}, Z = 2, $\mu_{(\mathrm{MoK}\alpha)}$ = 0.43 cm^{-1}; $F(000)$ = 420.00; number of reflections measured, 3818; number of unique reflections, 3818.

Structure Determination and Refinement. The structure was solved by direct method, using the crystallographic program system SHELX (Sheldrick, 1976).[9] The solution was based on 447 reflections with $E \geq 1.2$. All the nonhydrogen atoms, except those of the carbethoxy chain, were positioned from the first E map. Subsequent Fourier difference map revealed the remaining nonhydrogen and hydrogen atoms. Finally, three cycles of refinement, by full-matrix least-squares method, using 2438 reflections with $F_o > 2.2\sigma(F_o)$, with anisotropic temperature factors for the heterocyclic carbon atoms and C(13)–O(14) carboxylic group, isotropic temperature factors for all remaining nonhydrogen atoms, gave an R value of 0.088. The thermal parameters for hydrogen atoms were fixed. The weighting scheme was as follows: $w = 5.2179/[\sigma(F_o)^2 + 0.000855F_o^2]$. Drawings were made with PLUTO (Motherwell, 1976).[10]

Acknowledgment. This work was supported by the financial assistance from the Consiglio Nazionale delle Ricerche (Roma). We gratefully acknowledge Professor Giuseppe Zanotti, University of Padova, for intensity data collection.

Registry No. 1a, 25769-36-2; **1b**, 51849-76-4; **1c**, 25769-31-7; **2** (R$_4$ = R$_5$ = CH$_3$), 123-54-6; **2** (R$_4$ = C$_2$H$_5$O; R$_5$ = CH$_3$), 141-97-9; **2** (R$_4$ = R$_5$ = –(CH$_2$)$_3$–), 504-02-9; **4a**, 80049-04-3; **4b**, 80049-05-4; **4c**, 80049-06-5; **4d**, 80049-07-6; **4e**, 80049-08-7; copper(II) chloride, 7447-39-4.

Supplementary Material Available: Table I, full X-ray data for compound **4b**, fractional coordinates for the nonhydrogen atoms with estimated standard deviations; Table II, fractional coordinates for the hydrogen atoms with estimated standard deviations; Table III, thermal parameters for the nonhydrogen atoms with estimated standard deviations; Table IV, bond lengths involving nonhydrogen atoms with estimated standard deviations; Table V, bond lengths involving hydrogen atoms with estimated standard deviations; Table VI, bond angles involving nonhydrogen atoms with estimated standard deviations; Table VII, deviations from the plane formed by N(1), C(2), C(3), C(4), and C(5); Table VIII, angles between the normals to the planes; Figure 2, crystal packing (9 pages). Ordering information is given on any current masthead page.

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(9) G. M. Sheldrick, "A Program for Crystal Structure Determination", University Chemical Laboratory, Cambridge, England, 1976.

(10) W. D. S. Motherwell, Crystallographic Data Centre Manual, Cambridge, England, 1976.