Conjugated Azoalkenes. Part 14.[6] Synthesis of New 1-Amino- and 1,2-Diaminopyrrole Derivatives by Reaction of some Conjugated Azoalkenes with Activated Methylene Compounds RCH_2Ac and RCH_2CN (R = Aryl, Heteroaryl)

Orazio A. Attanasi,[a] Zhiyuan Liao,[b] Alexander McKillop,[c] Stefania Santeusanio[a] and Franco Serra-Zanetti[a]

[a] *Istituto di Chimica Organica della Facoltà di Scienze, Universita di Urbino, Piazza della Repubblica 13, 61029 Urbino, Italy*

[b] *Department of Chemical Engineering, Beijing Institute of Technology, 100081 Beijing, China*

[c] *School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK*

1-Amino- and 1,2-diamino-pyrrole derivatives are obtained in high yield by reaction of conjugated azoalkenes with ketones and cyanides containing methylene groups further activated by a 4-nitrophenyl, 2-fluorophenyl, benzothiazol-2-yl or benzimidazol-2-yl group. In some cases the heterocycles can be prepared in a one flask procedure, while in others a two step sequence is required, namely, formation of the 1,4-conjugate adduct and then cyclization. Reaction of 2,4-dichloro- and 2,3,6-trichlorophenylacetonitrile with the azoalkenes gave the 1,4-conjugate adducts, but these could not be successfully cyclized.

Conjugated azoalkenes react readily with a variety of substrates containing activated methylene or methine groups to give 1,4-conjugate addition products. The adducts thus formed from β-diketones, β-keto esters, β-keto amides, β-keto sulfones, β-dinitriles, β-cyano ketones, β-cyano esters and β-cyano amides undergo smooth heterocyclization to 1-aminopyrroles, 1-amino-2-hydroxy-2,3-dihydropyrroles and pyrrolo[2,3-*b*]pyrroles. In general, cyclization proceeds by initial nucleophilic attack at a ketone or cyano group.[1–6] Recently, however, we have found instances in which the heterocyclization unexpectedly proceeded by nucleophilic attack at an ester carbonyl group rather than at a cyano group, resulting in formation of 1-amino-2-oxo-2,3-dihydropyrroles.[6,7]

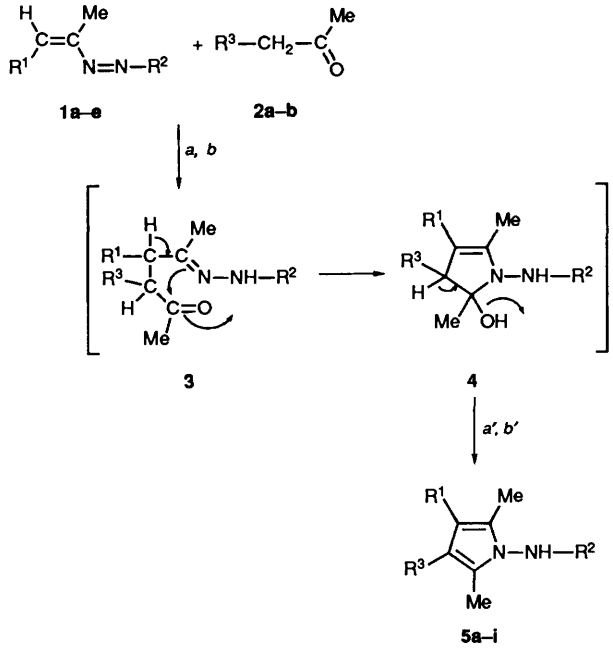
All of our studies thus far have involved highly activated methylene or methine groups of the type CH_2XY or RCHXY, where X and/or Y is carbonyl, sulfonyl or cyano. We now report an extension of these studies to an investigation of the reactions of conjugated azoalkenes with methylene groups of the type RCH_2Ac and RCH_2CN, where R is an electron-withdrawing aromatic or heteroaromatic group.

Results and Discussion

The reactions investigated were the condensation of azoalkenes **1a–e** with 4-nitrophenylacetone **2a**, 2-fluorophenylacetone **2b**, 4-nitrophenylacetonitrile **2c**, benzothiazol-2-ylacetonitrile **2d**, benzimidazol-2-ylacetonitrile **2e**, 2,4-dichlorophenylacetonitrile **2f** and 2,3,6-trichlorophenylacetonitrile **2g**, and two patterns of reactivity were discerned. With the ketones **2a**, **b** reaction led directly to 1-aminopyrroles **5a–i**, and neither 1,4-conjugate addition products **3** nor 2-hydroxy-2,3-dihydropyrrole intermediates **4** could be isolated (Scheme 1). With the nitriles **2c–g** the 1,4-conjugate adducts **3a–m** could be isolated easily and in high yield. Subsequent heterocyclization of **3a–k** gave the 1,2-diaminopyrroles **5j–t** (Scheme 2).

Thus, reaction of the conjugated azoalkenes **1a–e** with 4-nitrophenylacetone **2a** took place smoothly in methanol at room temperature in the presence of a catalytic amount of triethylamine. When all of the azoalkene had reacted (TLC), catalytic amounts of trifluoroacetic acid and copper dichloride dihydrate were added and the 1-amino-3-(4-nitrophenyl)pyrroles **5a–e** were obtained in excellent yield within 2–2.5 h. Reaction of **1a–e** with 2-fluorophenylacetone was found to proceed best in dimethyl sulfoxide in the presence of a catalytic amount of potassium *tert*-butoxide. Again, reaction proceeded smoothly at room temperature, and addition of catalytic amounts of trifluoroacetic acid and copper dichloride dihydrate after all of the azoalkene had reacted (TLC) gave good yields of the 1-amino-3-(2-fluorophenyl)pyrroles **5f–i**. Attempts to isolate intermediates **3** and **4** from these reactions were unsuccessful, in contrast to previous work where adducts analogous to **3**[1] and stable 2-hydroxy-2,3-dihydropyrroles analogous to **4** had been isolated and characterized.[2,3,6] Yield data for the preparation of the 3-aryl-1-aminopyrroles **5a–i** are given in Table 1.

Reaction of the azoalkenes **1a–e** with 4-nitrophenylacetonitrile **2c** took place readily at 0–5 °C in ethyl acetate containing a catalytic amount of triethylamine, and gave the conjugate

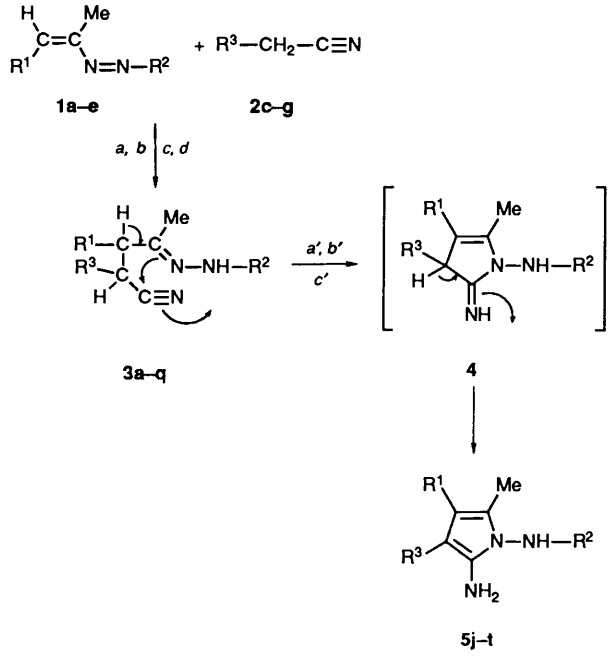


Scheme 1 *Reagents and conditions:* **2a**: *a*, MeOH, Et_3N, room temp., 0.5 h; *a*, MeOH, CF_3CO_2H, $CuCl_2{\cdot}2H_2O$, room temp., 1.5–2 h (see Table 1); **2b**: *b'*, DMSO, Bu'OK, room temp., 0.5 h; *b*, CF_3CO_2H, $CuCl_2{\cdot}2H_2O$, room temp., 2 h

Table 1 Yield and reaction times for the synthesis of 1-amino-3-(4-nitrophenyl)pyrroles **5a–e** and 1-amino-3-(2-fluorophenyl)pyrroles **5f–i**

Starting materials					Product	Reaction	
1	R^1	R^2	2	R^3[b]	5	time *t*/h	Yield (%)[a]
1a	CO_2Me	CO_2Me	**2a**	NP	**5a**	2.5	94
1b	CO_2Me	$CONH_2$	**2a**	NP	**5b**	2.5	91
1c	CO_2Et	$CONH_2$	**2a**	NP	**5c**	2.5	92
1d	CO_2Me	CONHPh	**2a**	NP	**5d**	2.0	90
1e	CO_2Et	CONHPh	**2a**	NP	**5e**	2.0	93
1a	CO_2Me	CO_2Me	**2b**	FP	**5f**	2.5	64
1b	CO_2Me	$CONH_2$	**2b**	FP	**5g**	2.5	77
1c	CO_2Et	$CONH_2$	**2b**	FP	**5h**	2.5	92
1d	CO_2Me	CONHPh	**2b**	FP	**5i**	2.5	75

[a] Yield of pure isolated product. [b] NP = 4-nitrophenyl; FP = 2-fluorophenyl.



Scheme 2 *Reagents and conditions:* **2c**: *a*, AcOEt, Et_3N, 0–5 °C, 1.5 h; *a*′, THF, H_2SO_4, room temp., 48–60 h (see Table 2); **2d**: *b*, AcOEt, Et_3N, room temp., 1.5 h; *b*′, MeOH, NaH, room temp., 2 h; **2e**: *c*, THF, MeONa, room temp., 1.5 h; *c*′, MeOH, NaH, room temp., 2; **2f** and **2g**: *d*, THF, MeONa, room temp., 2 h

adducts **3a–e** in excellent yield (Table 2). Efficient cyclization of **3a–e** to the 1,2-diamino-3-(4-nitrophenyl)pyrroles **5j–h** was achieved by treatment with concentrated sulfuric acid in THF at room temperature. The azoalkenes **1b–e** gave the adducts **3f–i** in the same way on treatment with benzothiazol-2-ylacetonitrile **2d**. Cyclization of **3f–i** to **5o–r** was found to proceed most rapidly and effectively when the adducts were treated with sodium methoxide prepared *in situ* from sodium hydride and methanol. In the cases of the azoalkenes **1b, c**, reaction at room temperature with benzimidazol-2-ylacetonitrile **2f** in THF containing a catalytic amount of sodium methoxide gave first the conjugate adducts **3j, k**. Further treatment of **3j, k** with freshly prepared sodium methoxide gave the 1,2-diamino-3-(benzimidazol-2-yl)pyrroles **5s, t**. The conjugate adducts **3l–o** and **3p, q** were easily obtained in excellent yield from condensation of the azoalkenes **1a–d** and **1b, c** with 2,4-dichlorophenylacetonitrile **2f** and 2,3,6-trichlorophenylacetonitrile **2g** respectively. However, all attempts to cyclize these adducts were unsuccessful, and only intractable mixtures were obtained. Experimental data for the preparation of the 1,4-conjugate adducts **3a–q**, 1,2-diamino-3-(4-nitrophenyl)pyrroles **5j–n**, 1,2-diamino-3-(benzothiazol-2-yl)pyrroles **5o–r** and 1,2-diamino-3-(benzimidazol-2-yl)pyrroles **5s, t** are summarised in Table 2.

The reaction sequence outlined in Scheme 2 is in good agreement with our previous findings in which we demonstrated that, depending on the molar ratios of reagents, 1,2-diaminopyrroles or pyrrolo[2,3-*b*]pyrroles may be obtained from the reactions of conjugated azoalkenes with nitriles containing highly activated methylene groups (β-dinitriles, β-cyano esters, β-cyano amides, β-cyano ketones).[4,5] Formation of pyrrolo-[2,3-*b*]pyrroles results from double 1,4-conjugate addition of the activated nitriles to the azo-ene system followed by double heterocyclization. Attempts to carry out similar reactions with the ketones **2a, b** and the nitriles **2c–g** were unsuccessful. In certain cases the initially formed adducts **3** appeared to react further with added azoalkene to give bis-adducts but attempted cyclization to pyrrolopyrroles gave complicated reaction mixtures.

Experimental

Alkoxycarbonylazoalkene[8] **1a** and aminocarbonylazoalkenes[9] **1b–e** were synthesized as previously reported. 4-Nitrophenylacetone **2a**, 2-fluorophenylacetone **2b**, 4-nitrophenylacetonitrile **2c**, benzothiazol-2-ylacetonitrile **2d**, benzimidazol-2-ylacetonitrile **2e**, 2,4-dichlorophenylacetonitrile **2f**, and 2,3,6-trichlorophenylacetonitrile **2g** were commercial materials (Lancaster) and were used without further purification. M.p.s were determined in capillary tubes with a Buechi apparatus, and are uncorrected. The products often decomposed at the m.p. All yields refer to pure isolated products. All IR spectra were obtained for Nujol mulls and were recorded on a Perkin-Elmer 298 spectrophotometer. All ^1H NMR spectra were recorded on a Varian EM-360L (60 MHz) and on a Bruker AC-200 (200 MHz) spectrometer in $(CD_3)_2SO$ solution. Chemical shifts (δ) are reported in ppm downfield from internal $SiMe_4$. *J*-Values in Hz. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; D_2O-exch., D_2O exchange. Macherey-Nagel precoated silica gel SIL G-25 UV_{254} plates (0.25 mm) were employed for analytical thin-layer chromatography (TLC), and Baker silica gel (0.063–0.200 mm) for column chromatography. All compounds prepared gave satisfactory elemental analyses (C ± 0.4, H ± 0.4, N ± 0.3%).

Typical Procedure for the Synthesis of 1-*Amino*-3-(4-*nitrophenyl*)*pyrroles* **5a–e**.—The azoalkene **1a–e** (1 mmol) was added at room temperature to a magnetically stirred solution of 4-nitrophenylacetone **2a** (1 mmol) in methanol (10 cm^3) which had previously been magnetically stirred at room temperature for 0.2 h with triethylamine (one drop). After the azoalkene **1a–e** disappeared (checked by TLC, *ca.* 0.3 h), to the reaction solution were added methanol (50 cm^3), trifluoroacetic acid

Table 2 Yield and reaction times for the synthesis of 1,4-conjugate adducts **3a–q**, 1,2-diamino-3-(4-nitrophenyl)pyrroles **5j–n**, 1,2-diamino-3-(benzothiazol-2-yl)pyrroles **5o–r**, and 1,2-diamino-3-(benzimidazol-2-yl)pyrroles **5s–t**

Starting materials					Products		Reaction time, *t*/h		Yield (%)[a]	
1	R^1	R^2	2	R^3[b]	3	5	3	5	3	5
1a	CO_2Me	CO_2Me	**2c**	NP	**3a**	**5j**	1.5	48.0	79	90
1b	CO_2Me	$CONH_2$	**2c**	NP	**3b**	**5k**	1.5	60.0	99	89
1c	CO_2Et	$CONH_2$	**2c**	NP	**3c**	**5l**	1.5	60.0	99	85
1d	CO_2Me	CONHPh	**2c**	NP	**3d**	**5m**	1.5	50.0	99	91
1e	CO_2Et	CONHPh	**2c**	NP	**3e**	**5n**	1.5	48.0	95	90
1b	CO_2Me	$CONH_2$	**2d**	BT	**3f**	**5o**	1.5	2.0	84	86
1c	CO_2Et	$CONH_2$	**2d**	BT	**3g**	**5p**	1.5	2.0	81	76
1d	CO_2Me	CONHPh	**2d**	BT	**3h**	**5q**	1.5	2.0	66	85
1e	CO_2Et	CONHPh	**2d**	BT	**3i**	**5r**	1.5	2.0	67	82
1b	CO_2Me	$CONH_2$	**2e**	BI	**3j**	**5s**	1.5	2.0	76	70
1c	CO_2Et	$CONH_2$	**2e**	BI	**3k**	**5t**	1.5	2.0	78	66
1a	CO_2Me	CO_2Me	**2f**	DCP	**3l**		2.0		72	
1b	CO_2Me	$CONH_2$	**2f**	DCP	**3m**		2.0		91	
1c	CO_2Et	$CONH_2$	**2f**	DCP	**3n**		2.0		91	
1d	CO_2Me	CONHPh	**2f**	DCP	**3o**		2.0		74	
1b	CO_2Me	$CONH_2$	**2g**	TCP	**3p**		2.0		75	
1c	CO_2Et	$CONH_2$	**2g**	TCP	**3q**		2.0		81	

[a] Yield of pure isolated product. [b] NP = nitrophenyl; BT = benzothiazol-2-yl; BI = benzimidazol-2-yl; DCP = 2,4-dichlorophenyl; TCP = 2,3,6-trichlorophenyl.

(two drops) and copper dichloride dihydrate (0.1 mmol). The mixture was magnetically stirred at room temperature for the appropriate reaction time (see Table 1) and checked by TLC (only one spot as major component). In the cases of the reaction of azoalkenes **1b–e**, the 1-aminopyrroles **5b–e** precipitated directly from the solution after partial evaporation under reduced pressure to about 5–10 cm^3, and were collected by filtration. Further reaction product was obtained from the filtrate by column chromatography on silica gel (ethyl acetate–cyclohexane mixtures). The products thus obtained were crystallized from ethyl acetate–cyclohexane. In the case of azoalkene **1a**, after complete evaporation of the solvent under reduced pressure, the residue was dissolved in ethyl acetate (50 cm^3). The resulting solution was washed with aqueous 1% sulfuric acid (2 × 20 cm^3), and with water (2 × 20 cm^3), then dried with sodium sulfate, concentrated under reduced pressure, and the residue separated by column chromatography on silica gel (cyclohexane–ethyl acetate mixtures). The 1-aminopyrrole **5a** was crystallized from ether–light petroleum (40–60 °C).

4-*Methoxycarbonyl*-1-*methoxycarbonylamino*-2,5-*dimethyl*-3-(4-*nitrophenyl*)*pyrrole* **5a**. M.p. 176–177 °C; ν_{max}/cm^{-1} 3215, 1710, 1600, 1547, 1512, 1350 and 1270; δ_H 2.0 (3 H, s, Me), 2.3 (3 H, s, Me), 3.5 (3 H, s, CO_2Me), 3.7 (3 H, s, CO_2Me), 7.4 (2 H, d, *J* 9, Ar), 8.2 (2 H, d, *J* 9, Ar) and 10.7 (1 H, s, NH, D_2O-exch.) (Found: C, 55.5; H, 4.7; N, 12.3. $C_{16}H_{17}N_3O_6$ requires C, 55.3; H, 4.9; N, 12.1%).

4-*Methoxycarbonyl*-2,5-*dimethyl*-3-(4-*nitrophenyl*)-1-*ureidopyrrole* **5b**. M.p. 284–286 °C; ν_{max}/cm^{-1} 3494, 3316, 3204, 1707, 1674, 1596, 1578, 1498, 1346 and 1160; δ_H 2.0 (3 H, s, Me), 2.3 (3 H, s, Me), 3.5 (3 H, s, CO_2Me), 6.4 (2 H, s, NH_2, D_2O-exch.), 7.4 (2 H, d, *J* 9, Ar), 8.2 (2 H, d, *J* 9, Ar) and 9.3 (1 H, s, NH, D_2O-exch.) (Found: C, 54.0; H, 4.9; N, 17.1. $C_{15}H_{16}N_4O_5$ requires C, 54.2; H, 4.8; N, 16.9%).

4-*Ethoxycarbonyl*-2,5-*dimethyl*-3-(4-*nitrophenyl*)-1-*ureidopyrrole* **5c**. M.p. 247–249 °C; ν_{max}/cm^{-1} 3410, 3260, 3210, 1692, 1675, 1590, 1550, 1514, 1342 and 1170; δ_H 1.0 (3 H, t, *J* 7, $CO_2CH_2\mathit{Me}$), 2.0 (3 H, s, Me), 2.3 (3 H, s, Me), 4.0 (2 H, q, *J* 7, $CO_2C\mathit{H}_2Me$), 6.4 (2 H, s, NH_2, D_2O-exch.), 7.4 (2 H, d, *J* 9, Ar), 8.2 (2 H, d, *J* 9, Ar) and 9.3 (1 H, s, NH, D_2O-exch.) (Found: C, 55.7; H, 5.0; N, 16.0. $C_{16}H_{18}N_4O_5$ requires C, 55.5; H, 5.2; N, 16.2%).

4-*Methoxycarbonyl*-2,5-*dimethyl*-3-(4-*nitrophenyl*)-1-*phenylureidopyrrole* **5d**. M.p. 249–251 °C; ν_{max}/cm^{-1} 3270, 1695, 1642, 1596, 1566, 1500 and 1352; δ_H 2.0 (3 H, s, Me), 2.4 (3 H, s, Me), 3.6 (3 H, s, CO_2Me), 6.9–7.5 (7 H, m, Ph and Ar), 8.2 (2 H, d, *J* 9, Ar), 9.4 (1 H, s, NH, D_2O-exch.) and 9.5 (1 H, s, NH, D_2O-exch.) (Found: C, 61.6; H, 5.1; N, 13.9. $C_{21}H_{20}N_4O_5$ requires C, 61.8; H, 4.9; N, 13.7%).

4-*Ethoxycarbonyl*-2,5-*dimethyl*-3-(4-*nitrophenyl*)-1-*phenylureidopyrrole* **5e**. M.p. 244–245 °C; ν_{max}/cm^{-1} 3260, 1710, 1640, 1595, 1560, 1512, 1345 and 1154; δ_H 1.1 (3 H, t, *J* 7, $CO_2CH_2\mathit{Me}$), 2.0 (3 H, s, Me), 2.4 (3 H, s, Me), 4.0 (2 H, q, *J* 7, $CO_2C\mathit{H}_2Me$), 6.9–7.5 (7 H, m, Ph and Ar), 8.2 (2 H, d, *J* 9, Ar), 9.4 (1 H, s, NH, D_2O-exch.) and 9.5 (1 H, s, NH, D_2O-exch.) (Found: C, 62.8; H, 4.9; N, 13.1. $C_{22}H_{22}N_4O_5$ requires C, 62.5; H, 5.2; N, 13.3%).

Typical Procedure for the Synthesis of 1-*Amino*-3-(2-*fluorophenyl*)*pyrroles* **5f–i**.—The azoalkene **1a–d** (2 mmol) was added at room temperature to a magnetically stirred solution of 2-fluorophenylacetone **2b** (3 mmol) in dimethyl sulfoxide (2 cm^3) which had previously been magnetically stirred at room temperature for 0.2 h with potassium *tert*-butoxide (0.1 mmol). After the azoalkene **1a–d** disappeared (checked by TLC, about 0.5 h), to the reaction solution were added trifluoroacetic acid (three drops) and copper dichloride dihydrate (0.1 mmol). The mixture was magnetically stirred at room temperature for 2 h, then ethyl acetate (100 cm^3) was added. The organic phase was washed with aqueous 1% sulfuric acid (2 × 20 cm^3) and with water (2 × 20 cm^3), dried with sodium sulfate, concentrated under reduced pressure, and then separated by column chromatography on silica gel (cyclohexane–ethyl acetate mixtures). The 1-aminopyrroles **5f–i** were crystallized from ethyl acetate–cyclohexane or ether–light petroleum (40–60 °C).

3-(2-*Fluorophenyl*)-4-*methoxycarbonyl*-1-*methoxycarbonylamino*-2,5-*dimethylpyrrole* **5f**. M.p. 112–114 °C; ν_{max}/cm^{-1} 3240, 1750, 1680, 1550 and 1250; δ_H 1.9 (3 H, s, Me), 2.3 (3 H, s, Me), 3.5 (3 H, s, CO_2Me), 3.7 (3 H, s, CO_2Me). 7.1–7.4 (4 H, m, Ar) and 10.7 (1 H, s, NH, D_2O-exch.) (Found: C, 59.9; H, 5.4; N, 8.8. $C_{16}H_{17}FN_2O_4$ requires C, 60.0; H, 5.3; N, 8.7%).

3-(2-*Fluorophenyl*)-4-*methoxycarbonyl*-2,5-*dimethyl*-1-*ureidopyrrole* **5g**. M.p. 189–191 °C; ν_{max}/cm^{-1} 3460, 3240, 3130, 1710, 1680, 1600, 1545 and 1290; δ_H 1.9 (3 H, s, Me), 2.3 (3 H, s, Me), 3.5 (3 H, s, CO_2Me), 6.3 (2 H, s, NH_2, D_2O-exch.), 7.1–

7.4 (2 H, m, Ar), and 9.2 (1 H, s, NH, D_2O-exch.) (Found: C, 59.2; H, 5.2; N, 13.7. $C_{15}H_{16}FN_3O_3$ requires C, 59.0; H, 5.3; N, 13.8%).

4-Ethoxycarbonyl-3-(2-fluorophenyl)-2,5-dimethyl-1-ureidopyrrole **5h**. M.p. 150–152 °C; ν_{max}/cm^{-1} 3415, 3320, 3200, 1680, 1585, 1540, 1280 and 1170; δ_H 1.0 (3 H, t, *J* 7, CO_2CH_2Me), 1.9 (3 H, s, Me), 2.3 (3 H, s, Me), 3.9 (2 H, q, *J* 7, CO_2CH_2Me), 6.3 (2 H, s, NH_2, D_2O-exch.), 7.1–7.4 (4 H, m, Ar) and 9.2 (1 H, s, NH, D_2O-exch.) (Found: C, 60.4; H, 5.5; N, 13.0. $C_{16}H_{18}FN_3O_3$ requires C, 60.2; H, 5.7; N, 13.2%).

3-(2-Fluorophenyl)-4-methoxycarbonyl-2,5-dimethyl-1-phenylureidopyrrole **5i**. M.p. 209–211 °C; ν_{max}/cm^{-1} 3360, 1724, 1660, 1600, 1540, 1310, 1200 and 1168; δ_H 2.0 (3 H, s, Me), 2.4 (3 H, s, Me), 3.5 (3 H, s, CO_2Me), 6.9–7.6 (9 H, m, Ph and Ar), 9.3 (1 H, s, NH, D_2O-exch.) and 9.4 (1 H, s, NH, D_2O-exch.) (Found: C, 66.3; H, 5.1; N, 11.0. $C_{21}H_{20}FN_3O_3$ requires C, 66.1; H, 5.3; N, 11.0%).

Typical Procedure for the Synthesis of 2-(α-Cyano-4-nitrobenzyl)acetoacetate Hydrazones **3a–e** *and 1,2-Diamino-3-(4-nitrophenyl)pyrroles* **5j–n**.—The azoalkene **1a–e** (2 mmol) was added in small portions (about 0.3 h) at 0–5 °C to a magnetically stirred solution of 4-nitrophenylacetonitrile **2c** (4 mmol) in ethyl acetate (4 cm^3) which had previously been magnetically stirred for 0.2 h at 0–5 °C with triethylamine (one drop). Reaction was continued for 1 h under these conditions until the azoalkene **1a–e** had disappeared (checked by TLC). In the cases of the reactions of azoalkenes **1b–e**, the 1,4-conjugate adducts **3b–e** precipitated directly from the solution and were collected by filtration. In the case of azoalkene **1a**, after complete evaporation of the solvent under reduced pressure the residue was separated by column chromatography on silica gel (dichloromethane–ethyl acetate mixtures). The 1,4-conjugate adduct **3a** was crystallized from ethyl acetate–cyclohexane. To a magnetically stirred suspension of the 1,4-conjugate adducts **3a–e** in THF (3 cm^3) was added dropwise at 0 °C concentrated (98%) sulfuric acid (2 cm^3). The reaction mixture was magnetically stirred for the appropriate time (48–60 h, see Table 2) at room temperature, then added to ethyl acetate (100 cm^3) and the resulting mixture neutralized with saturated aqueous sodium hydrogen carbonate. The organic phase was separated, washed with water (2 × 20 cm^3), and dried with sodium sulfate. After partial evaporation of the solvent under reduced pressure at room temperature to about 2 cm^3, the 1,2-diaminopyrroles **5j–n** precipitated directly from the solution in good purity, and were collected by filtration under reduced pressure.

Methyl 2-(α-cyano-4-nitrobenzyl)acetoacetate methoxycarbonylhydrazone **3a**. M.p. 171–173 °C (decomp.); ν_{max}/cm^{-1} 3215, 3120, 2240, 1740, 1710, 1600, 1515 and 1350; δ_H 1.9 (3 H, s, Me), 3.5 (3 H, s, CO_2Me), 3.7 (3 H, s, CO_2Me), 4.3 (1 H, d, *J* 9, CH), 5.0 (1 H, d, *J* 9, CH), 7.8 (2 H, d, *J* 9, Ar), 8.2 (2 H, d, *J* 9, Ar) and 10.2 (1 H, s, NH, D_2O-exch.) (Found: C, 51.6; H, 4.5; N, 16.0. $C_{15}H_{16}N_4O_6$ requires C, 51.7; H, 4.6; N, 16.1%).

Methyl 2-(α-cyano-4-nitrobenzyl)acetoacetate aminocarbonylhydrazone **3b**. M.p. 161–163 °C (decomp.); ν_{max}/cm^{-1} 3490, 3370, 3190, 2245, 1740, 1686, 1585, 1518, 1345 and 1162; δ_H 1.8 (3 H, s, Me), 3.7 (3 H, s, CO_2Me), 4.3 (1 H, d, *J* 9, CH), 5.4 (1 H, d, *J* 9, CH), 6.4 (2 H, s, NH_2, D_2O-exch.), 7.8 (2 H, d, *J* 9, Ar), 8.2 (2 H, d, *J* 9, Ar) and 9.3 (1 H, s, NH, D_2O-exch.) (Found: C, 50.7; H, 4.2; N, 20.9. $C_{14}H_{15}N_5O_5$ requires C, 50.4; H, 4.5; N, 21.0%).

Ethyl 2-(α-cyano-4-nitrobenzyl)acetoacetate aminocarbonylhydrazone **3c**. M.p. 136–138 °C (decomp.); ν_{max}/cm^{-1} 3470, 3350, 3185, 2244, 1738, 1680, 1590, 1520, 1340, 1230 and 1165; δ_H 1.1 (3 H, t, *J* 7, CO_2CH_2Me), 1.7 (3 H, s, Me), 4.1 (2 H, q, *J* 7, CO_2CH_2Me), 4.3 (1 H, d, *J* 9, CH), 5.4 (1 H, d, *J* 9, CH), 6.3 (2 H, s, NH_2, D_2O-exch.), 7.8 (2 H, d, *J* 9, Ar), 8.2 (2 H, d, *J* 9, Ar) and 9.2 (1 H, s, NH, D_2O-exch.) (Found: C, 52.1; H, 4.7; N, 20.0. $C_{15}H_{17}N_5O_5$ requires C, 51.9; H, 4.9; N, 20.2%).

Methyl 2-(α-cyano-4-nitrobenzyl)acetoacetate phenylaminocarbonylhydrazone **3d**. M.p. 199–200 °C (decomp.); ν_{max}/cm^{-1} 3360, 3190, 3080, 2245, 1740, 1675, 1600, 1540, 1520 and 1340; δ_H 1.9 (3 H, s, Me), 3.6 (3 H, s, CO_2Me), 4.3 (1 H, d, *J* 9, CH), 5.4 (1 H, d, *J* 9, CH), 7.0–7.6 (5 H, m, Ph), 7.8 (2 H, d, *J* 9, Ar), 8.2 (2 H, d, *J* 9, Ar), 8.6 (1 H, s, NH, D_2O-exch.) and 9.9 (1 H, s, NH, D_2O-exch.) (Found: C, 58.5; H, 4.8; N, 17.3 $C_{20}H_{19}N_5O_5$ requires C, 58.7; H, 4.7; N, 17.1%).

Ethyl 2-(α-cyano-4-nitrobenzyl)acetoacetate phenylaminocarbonylhydrazone **3e**. M.p. 205–206 °C (decomp.); ν_{max}/cm^{-1} 3360, 3190, 3080, 2244, 1736, 1677, 1595, 1535, 1520 and 1340; δ_H 1.1 (3 H, t, *J* 7, CO_2CH_2Me), 1.9 (3 H, s, Me), 4.0 (2 H, q, *J* 7, CO_2CH_2Me), 4.3 (1 H, d, *J* 9, CH), 5.4 (1 H, d, *J* 9, CH), 6.9–7.6 (5 H, m, Ph), 7.8 (2 H, d, *J* 9, Ar), 8.2 (2 H, d, *J* 9, Ar), 8.6 (1 H, s, NH, D_2O-exch.) and 9.9 (1 H, s, NH, D_2O-exch.) (Found: C, 59.8; H, 4.9; N, 16.4. $C_{21}H_{21}N_5O_5$ requires C, 59.6; H, 5.0; N, 16.5%).

2-Amino-4-methoxycarbonyl-1-methoxycarbonylamino-5-methyl-3-(4-nitrophenyl)pyrrole **5j**. M.p. 198–200 °C; ν_{max}/cm^{-1} 3310, 3210, 1730, 1680, 1620, 1565, 1505, 1340 and 1280; δ_H 2.2 (3 H, s, Me), 3.6 (3 H, s, CO_2Me), 3.7 (3 H, s, CO_2Me), 5.2 (2 H, s, NH_2, D_2O-exch.), 7.4 (2 H, d, *J* 9, Ar), 8.1 (2 H, d, *J* 9, Ar) and 10.3 (1 H, s, NH, D_2O-exch.) (Found: C, 51.9; H, 4.5; N, 15.9. $C_{15}H_{16}N_4O_6$ requires C, 51.7; H, 4.6; N, 16.1%).

2-Amino-4-methoxycarbonyl-5-methyl-3-(4-nitrophenyl)-1-ureidopyrrole **5k**. M.p. 219–221 °C; ν_{max}/cm^{-1} 3420, 3320, 3200, 1680, 1600, 1550, 1510 and 1340; δ_H 2.2 (3 H, s, Me), 3.6 (3 H, s, CO_2Me), 4.9 (2 H, s, NH_2, D_2O-exch.), 6.4 (2 H, s, NH_2, D_2O-exch.), 7.4 (2 H, d, *J* 9, Ar), 8.1 (2 H, d, *J* 9, Ar) and 9.0 (1 H, s, NH, D_2O-exch.) (Found: C, 50.6; H, 4.3; N, 20.8. $C_{14}H_{15}N_5O_5$ requires C, 50.4; H, 4.5; N, 21.0%).

2-Amino-4-ethoxycarbonyl-5-methyl-3-(4-nitrophenyl)-1-ureidopyrrole **5l**. M.p. 206–208 °C; ν_{max}/cm^{-1} 3420, 3340, 3200, 1680, 1590, 1545, 1490 and 1340; δ_H 1.1 (3 H, t, *J* 7, CO_2CH_2Me), 2.3 (3 H, s, Me), 4.1 (2 H, d, *J* 7, CO_2CH_2Me), 4.8 (2 H, s, NH_2, D_2O-exch.), 6.3 (2 H, s, NH_2, D_2O-exch.), 7.1 (2 H, d, *J* 9, Ar), 8.2 (2 H, d, *J* 9, Ar) and 9.0 (1 H, s, NH, D_2O-exch.) (Found: C, 51.7; H, 5.1; N, 20.4. $C_{15}H_{17}N_5O_5$ requires C, 51.9; H, 4.9; N, 20.2%).

2-Amino-4-methoxycarbonyl-5-methyl-3-(4-nitrophenyl)-1-phenylureidopyrrole **5m**. M.p. 209–210 °C; ν_{max}/cm^{-1} 3440, 3350, 3260, 1710, 1650, 1595, 1560, 1495, 1330 and 1195; δ_H 2.3 (3 H, s, Me), 3.7 (3 H, s, CO_2Me), 5.0 (2 H, s, NH_2, D_2O-exch.), 7.0–7.6 (7 H, m, Ph and Ar), 8.2 (2 H, d, *J* 9, Ar), 9.2 (1 H, s, NH, D_2O-exch.) and 9.3 (1 H, s, NH, D_2O-exch.) (Found: C, 58.5; H, 4.9; N, 17.3. $C_{20}H_{19}N_5O_5$ requires C, 58.7; H, 4.7; N, 17.1%).

2-Amino-4-ethoxycarbonyl-5-methyl-3-(4-nitrophenyl)-1-phenylureidopyrrole **5n**. M.p. 203–205 °C; ν_{max}/cm^{-1} 3435, 3350, 3260, 1700, 1650, 1590, 1555, 1490, 1335 and 1180; δ_H 1.1 (3 H, t, *J* 7, CO_2CH_2Me), 2.3 (3 H, s, Me), 4.1 (2 H, q, *J* 7, CO_2CH_2Me), 5.1 (2 H, s, NH_2, D_2O-exch.), 7.0–7.5 (7 H, m, Ph and Ar), 8.1 (2 H, d, *J* 9, Ar), 9.2 (1 H, s, NH, D_2O-exch.) and 9.3 (1 H, s, NH, D_2O-exch.) (Found: C, 59.8; H, 4.8; N, 16.3. $C_{21}H_{21}N_5O_5$ requires C, 59.6; H, 5.0; N, 16.5%).

Typical Procedure for the Synthesis of 2-[(Benzothiazol-2-yl)cyanomethyl]acetoacetate Hydrazones **3f–i** *and 3-(Benzothiazol-2-yl)-1,2-diaminopyrroles* **5o–r**.—The azoalkene **1b–e** (2 mmol) was added in small portions (about 0.3 h) at room temperature to a magnetically stirred solution of benzothiazol-2-yl-acetonitrile **2d** (4 mmol) in ethyl acetate (5 cm^3) which had previously been magnetically stirred for 0.2 h at room temperature with triethylamine (one drop). Reaction was continued for 1 h under these conditions until the azoalkene **1b–e** had disappeared (checked by TLC). After complete

evaporation of the solvent under reduced pressure, the residue was separated by column chromatography on silica gel (cyclohexane–ethyl acetate or ethyl acetate–methanol mixtures). The 1,4-conjugate adducts **3f–i** were crystallized from ethyl acetate–cyclohexane. To a magnetically stirred solution of 1,4-conjugate adduct **3f–i** (1 mmol) in methanol (50 cm^3) was added at room temperature sodium hydride (0.1 mmol). The reaction mixture was magnetically stirred for 2 h until a precipitate had formed. After partial evaporation of the solvent under reduced pressure to *ca.* 3–5 cm^3, the 1,2-diaminopyrroles **5o–r** which separated were collected by filtration under reduced pressure and washed with ether.

Methyl 2-[(benzothiazol-2-yl)cyanomethyl]acetoacetate aminocarbonylhydrazone **3f**. M.p. 172–174 °C (decomp.); ν_{max}/cm^{-1} 3440, 3200, 2240, 1736, 1694, 1573, 1275 and 1225; δ_H 1.9 (3 H, s, Me), 3.7 (3 H, s, CO_2Me), 4.4 (1 H, d, *J* 9, CH), 5.9 (1 H, d, *J* 9, CH), 6.5 (2 H, s, NH_2, D_2O-exch.), 7.4–7.6 (2 H, m, Ar), 8.0–8.2 (2 H, m, Ar) and 9.4 (1 H, s, NH, D_2O-exch.) (Found: C, 52.0; H, 4.5; N, 20.5. $C_{15}H_{15}N_5O_3S$ requires C, 52.2; H, 4.4; N, 20.3%).

Ethyl 2-[(benzothiazol-2-yl)cyanomethyl]acetoacetate aminocarbonylhydrazone **3g**. M.p. 171–173 °C (decomp.); ν_{max}/cm^{-1} 3450, 3200, 2240, 1736, 1697, 1580, 1284 and 1230; δ_H 1.0 (3 H, t, *J* 7, CO_2CH_2Me), 1.9 (3 H, s, Me), 4.0 (2 H, q, *J* 7, CO_2CH_2Me), 4.4 (1 H, d, *J* 9, CH), 5.9 (1 H, d, *J* 9, CH), 6.5 (2 H, s, NH_2, D_2O-exch.), 7.4–7.6 (2 H, m, Ar), 8.0–8.2 (2 H, m, Ar) and 9.5 (1 H, s, NH, D_2O-exch.) (Found: C, 53.7; H, 4.6; N, 19.3. $C_{16}H_{17}N_5O_3S$ requires C, 53.5; H, 4.8; N, 19.5%).

Methyl 2-[(benzothiazol-2-yl)cyanomethyl]acetoacetate phenylaminocarbonylhydrazone **3h**. M.p. 164–165 °C (decomp.); ν_{max}/ cm^{-1} 3388, 3200, 3090, 2240, 1735, 1700, 1590, 1530 and 1210; δ_H 2.0 (3 H, s, Me), 3.7 (3 H, s, CO_2Me), 4.6 (1 H, d, *J* 9, CH), 6.1 (1 H, d, *J* 9, CH), 7.0–8.1 (9 H, m, Ph and Ar), 8.6 (1 H, s, NH, D_2O-exch.) and 9.9 (1 H, s, NH, D_2O-exch.) (Found: C, 59.5; H, 4.7; N, 16.8. $C_{21}H_{19}N_5O_3S$ requires C, 59.8; H, 4.5; N, 16.6%).

Ethyl 2-(benzothiazol-2-yl)cyanomethyl]acetoacetate phenylaminocarbonylhydrazone **3i**. M.p. 158–160 °C (decomp.); ν_{max}/ cm^{-1} 3380, 3200, 3090, 2240, 1730, 1700, 1590, 1535 and 1214; δ_H 1.1 (3 H, t, *J* 7, CO_2CH_2Me), 2.0 (3 H, s, Me), 4.2 (2 H, q, *J* 7, CO_2CH_2Me), 4.5 (1 H, d, *J* 9, CH), 6.0 (1 H, d, *J* 9, CH), 7.0–8.1 (9 H, m, Ph and Ar), 8.7 (1 H, s, NH, D_2O-exch.) and 9.9 (1 H, s, NH, D_2O-exch.) (Found: C, 60.5; H, 5.1; N, 16.4. $C_{22}H_{21}N_5O_3S$ requires C, 60.7; H, 4.9; N, 16.1%).

2-Amino-3-(benzothiazol-2-yl)-4-methoxycarbonyl-5-methyl-1-ureidopyrrole **5o**. M.p. 218–220 °C; ν_{max}/cm^{-1} 3390, 3330, 3260, 3200. 1680, 1600, 1500 and 1200; δ_H 2.2 (3 H, s, Me), 3.8 (3 H, s, CO_2Me), 6.4 (2 H, s, NH_2, D_2O-exch.), 7.0 (2 H, s, NH_2, D_2O-exch.), 7.1–7.4 (2 H, m, Ar), 7.7–7.9 (2 H, m, Ar) and 9.1 (1 H, s, NH, D_2O-exch.) (Found: C, 52.4; H, 4.3; N, 20.2. $C_{15}H_{15}N_5O_3S$ requires C, 52.2; H, 4.4; N, 20.3%).

2-Amino-3-(benzothiazol-2-yl)-4-ethoxycarbonyl-5-methyl-1-ureidopyrrole **5p**. M.p. 215–217 °C; ν_{max}/cm^{-1} 3456, 3330, 3180, 1670, 1610, 1510 and 1200; δ_H 1.3 (3 H, t, *J* 7, CO_2CH_2Me), 2.3 (3 H, s, Me), 4.3 (2 H, q, *J* 7, CO_2CH_2Me), 6.4 (2 H, s, NH_2, D_2O-exch.), 7.0 (2 H, s, NH_2, D_2O-exch.), 7.1–7.4 (2 H, m, Ar), 7.7–7.9 (2 H, m, Ar) and 9.1 (1 H, s, NH, D_2O-exch.) (Found: C, 53.7; H, 4.6; N, 19.3. $C_{16}H_{17}N_5O_3S$ requires C, 53.5; H, 4.8; N, 19.5%).

2-Amino-3-(benzothiazol-2-yl)-4-methoxycarbonyl-5-methyl-1-phenylureidopyrrole **5q**. M.p. 217–219 °C; ν_{max}/cm^{-1} 3480, 3315, 3200, 1710, 1665, 1600, 1570, 1500 and 1195; δ_H 2.3 (3 H, s, Me), 3.8 (3 H, s, CO_2Me), 7.0 (1 H, m, Ph), 7.1 (2 H, s, NH_2, D_2O-exch.), 7.2–7.9 (8 H, m, Ph and Ar), 9.3 (1 H, s, NH, D_2O-exch.) and 9.4 (1 H, s, NH, D_2O-exch.) (Found: C, 60.0; H, 4.3; N, 16.4. $C_{21}H_{19}N_5O_3S$ requires C, 59.8; H, 4.5; N, 16.6%).

2-Amino-3-(benzothiazol-2-yl)-4-ethoxycarbonyl-5-methyl-1-phenylureidopyrrole **5r**. M.p. 210–212 °C; ν_{max}/cm^{-1} 3270, 1710, 1650, 1600, 1570, 1500 and 1194; δ_H 1.3 (3 H, t, *J* 7, CO_2CH_2Me), 2.3 (3 H, s, Me), 4.3 (2 H, q, *J* 7, CO_2CH_2Me), 7.0 (1 H, m, Ph), 7.1 (2 H, s, NH_2, D_2O-exch.), 7.2–7.9 (8 H, m, Ph and Ar), 9.3 (1 H, s, NH, D_2O-exch.) and 9.4 (1 H, s, NH, D_2O-exch.) (Found: C, 60.5; H, 5.1; N, 16.3. $C_{22}H_{21}N_5O_3S$ requires C, 60.7; H, 4.9; N, 16.1%).

Typical Procedure for the Synthesis of 2-[(Benzimidazol-2-yl)cyanomethyl]acetoacetate Hydrazones **3j–k** *and 3-(Benzimidazol-2-yl)-1,2-diaminopyrroles* **5s–t**. The azoalkene **1b–c** (2 mmol) was added in small portions (about 0.3 h) at room temperature to a magnetically stirred solution of benzimidazol-2-ylacetonitrile **2e** (4 mmol) in tetrahydrofuran (5 cm^3) which had previously been magnetically stirred for 0.2 h at room temperature with sodium methoxide (0.1 mmol). Reaction was continued for 1 h under these conditions until the azoalkene **1b–c** had disappeared (checked by TLC). After complete evaporation of the solvent under reduced pressure, the residue was separated by column chromatography on silica gel (ethyl acetate or ethyl acetate–methanol mixtures). The 1,4-conjugate adducts **3j–k** were crystallized from ethyl acetate–cyclohexane. To a magnetically stirred solution of 1,4-conjugate adduct **3j–k** (1 mmol) in methanol (50 cm^3) was added at room temperature sodium hydride (0.1 mmol). The reaction mixture was magnetically stirred for 2 h until a precipitate formed. After partial evaporation of the solvent under reduced pressure to about 3–5 cm^3, the 1,2-diaminopyrroles **5s–t** which separated were collected by filtration under reduced pressure and washed with ether.

Methyl 2-[(benzimidazol-2-yl)cyanomethyl]acetoacetate aminocarbonylhydrazone **3j**. M.p. 181–182 °C (decomp.); ν_{max}/ cm^{-1} 3400, 3350, 3300, 3240, 3160, 2245, 1735, 1666, 1580 and 1270; δ_H 2.0 (3 H, s, Me), 3.6 (3 H, s, CO_2Me), 4.4 (1 H, d, *J* 9, CH), 5.3 (1 H, d, *J* 9, CH), 6.5 (2 H, s, NH_2, D_2O-exch.), 7.2 (2 H, m, Ar), 7.5 (2 H, m, Ar), 9.4 (1 H, s, NH, D_2O-exch.) and 12.7 (1 H, s, NH, D_2O-exch.) (Found: C, 54.7; H, 4.8; N, 25.8. $C_{15}H_{16}N_6O_3$ requires C, 54.9; H, 4.9; N, 25.6%).

Ethyl 2-[(benzimidazol-2-yl)cyanomethyl]acetoacetate aminocarbonylhydrazone **3k**. M.p. 178–179 °C (decomp.); ν_{max}/cm^{-1} 3390, 3350, 3300, 3240, 3170, 2245, 1740, 1660, 1584 and 1180; δ_H 1.1 (3 H, t, *J* 7, CO_2CH_2Me), 1.9 (3 H, s, Me), 4.1 (2 H, q, *J* 7, CO_2CH_2Me), 4.3 (1 H, d, *J* 9, CH), 5.3 (1 H, d, *J* 9, CH), 6.5 (2 H, s, NH_2, D_2O-exch.), 7.2 (2 H, m, Ar), 7.5 (2 H, m, Ar), 9.4 (1 H, s, NH, D_2O-exch.) and 12.6 (1 H, s, NH, D_2O-exch.) (Found: C, 56.0; H, 5.4; N, 24.6. $C_{16}H_{18}N_6O_3$ requires C, 56.1; H, 5.3; N, 24.5%).

2-Amino-3-(benzimidazol-2-yl)-4-methoxycarbonyl-5-methyl-1-ureidopyrrole **5s**. M.p. 219–220 °C (decomp.); ν_{max}/cm^{-1} 3390, 3215, 3185, 1708, 1660, 1614, 1550, 1190 and 1100; δ_H 2.3 (3 H, s, Me), 3.9 (3 H, s, CO_2Me), 6.4 (2 H, s, NH_2, D_2O-exch.), 6.7 (2 H, s, NH_2, D_2O-exch.), 7.0 (2 H, m, Ar), 7.5 (2 H, m, Ar), 9.2 (1 H, s, NH, D_2O-exch.) and 12.3 (1 H, s, NH, D_2O-exch.) (Found: C, 54.9; H, 5.0; N, 25.5. $C_{15}H_{16}N_6O_3$ requires C, 54.9; H, 4.9; N, 25.6%).

2-Amino-3-(benzimidazol-2-yl)-4-ethoxycarbonyl-5-methyl-1-ureidopyrrole **5t**. M.p. 215–216 °C (decomp.); ν_{max}/cm^{-1} 3400, 3190, 1700, 1650, 1616, 1560, 1190 and 1110; δ_H 1.3 (3 H, t, *J* 7, CO_2CH_2Me), 2.3 (3 H, s, Me), 4.3 (2 H, q, *J* 7, CO_2CH_2Me), 6.4 (2 H, s, NH_2, D_2O-exch.), 6.7 (2 H, s, NH_2, D_2O-exch.), 7.0 (2 H, m, Ar), 7.5 (2 H, m, Ar), 9.1 (1 H, s, NH, D_2O-exch.) and 12.3 (1 H, s, NH, D_2O-exch.) (Found: C, 56.3; H, 5.2; N, 24.4. $C_{16}H_{18}N_6O_3$ requires C, 56.1; H, 5.3; N, 24.5%).

Typical Procedure for the Synthesis of 2-(2,4-Dichloro-α-cyanobenzyl)acetoacetate Hydrazones **3l–o** *and 2-(2,3,6-Trichloro-α-cyanobenzyl)acetoacetate Hydrazones* **3p–q**.—The azoalkene **1a–d** (1 mmol) was added in small portions (about 0.3 h) at room temperature to a magnetically stirred solution of

2,4-dichlorophenylacetonitrile **2f** (2 mmol) in tetrahydrofuran (2 cm^3) which had previously been magnetically stirred at room temperature for 0.2 h with sodium methoxide (0.1 mmol). Reaction was continued for 1.5 h under these conditions until the azoalkene **1a–d** had disappeared (checked by TLC). After complete evaporation of the solvent under reduced pressure, the residue was separated by column chromatography on silica gel (cyclohexane–ethyl acetate mixtures). The 1,4-conjugate adducts **3l–q** were crystallized from ethyl acetate–cyclohexane or dichloromethane–light petroleum (40–60 °C).

Methyl 2-(2,4-dichlorophenyl-α-cyanobenzyl)acetoacetate methoxycarbonylhydrazone **3l**. M.p. 150–153 °C (decomp.); ν_{max}/cm^{-1} 3220, 3110, 2245, 1740, 1700, 1260, 1220 and 1068; δ_H 1.8 (3 H, s, Me), 3.6 (3 H, s, CO_2Me), 3.7 (3 H, s, CO_2Me), 4.3 (1 H, d, *J* 10, CH), 5.0 (1 H, d, *J* 10, CH), 7.4–7.8 (3 H, m, Ar) and 10.0 (1 H, s, NH, D_2O-exch.) (Found: C, 48.2; H, 4.3; N, 11.4. $C_{15}H_{15}Cl_2N_3O_4$ requires C, 48.4; H, 4.1; N, 11.3%).

Methyl 2-(2,4-dichloro-α-cyanobenzyl)acetoacetate aminocarbonylhydrazone **3m**. M.p. 185–186 °C (decomp.); ν_{max}/cm^{-1} 3460, 3215, 2240, 1745, 1690, 1590, 1340 and 1165; δ_H 1.9 (3 H, s, Me), 3.5 (3 H, s, CO_2Me), 4.3 (1 H, d, *J* 10, CH), 5.2 (1 H, d, *J* 10, CH), 6.5 (2 H, s, NH_2, D_2O-exch.), 7.4–7.8 (3 H, m, Ar) and 9.5 (1 H, s, NH, D_2O-exch.) (Found: C, 47.0; H, 4.0; N, 15.8. $C_{14}H_{14}Cl_2N_4O_3$ requires C, 47.1; H, 3.9; N, 15.7%).

Ethyl 2-(2,4-dichloro-α-cyanobenzyl)acetoacetate aminocarbonylhydrazone **3n**. M.p. 175–176 °C (decomp.); ν_{max}/cm^{-1} 3460, 3200, 2240, 1735, 1690, 1570, 1260, 1175 and 1140; δ_H 1.1 (3 H, t, *J* 7, CO_2CH_2Me), 1.8 (3 H, s, Me), 4.1 (2 H, q, *J* 7, CO_2CH_2Me), 4.3 (1 H, d, *J* 10, CH), 5.2 (1 H, d, *J* 10, CH), 6.5 (2 H, s, NH_2, D_2O-exch.), 7.4–7.8 (3 H, m, Ar) and 9.2 (1 H, s, NH, D_2O-exch.) (Found: C, 48.7; H, 4.2; N, 15.0. $C_{15}H_{16}Cl_2N_4O_3$ requires C, 48.5; H, 4.3; N, 15.1%).

Methyl 2-(2,4-dichloro-α-cyanobenzyl)acetoacetate phenylaminocarbonylhydrazone **3o**. M.p. 187–189 °C (decomp.); ν_{max}/cm^{-1} 3350, 3200, 3080, 2240, 1740, 1680, 1590, 1530, 1275, 1220 and 1140; δ_H 1.9 (3 H, s, Me), 3.7 (3 H, s, CO_2Me), 4.2 (1 H, d, *J* 10, CH), 5.3 (1 H, d, *J* 10, CH), 6.9–7.8 (8 H, m, Ph and Ar), 8.6 (1 H, s, NH, D_2O-exch.) and 9.9 (1 H, s, NH, D_2O-exch.) (Found: C, 55.2; H, 4.4; N, 12.8. $C_{20}H_{18}Cl_2N_4O_3$ requires C, 55.4; H, 4.2; N, 12.9%).

Methyl 2-(2,3,6-trichloro-α-cyanobenzyl)acetoacetate aminocarbonylhydrazone **3p**. M.p. 187–189 °C (decomp.); ν_{max}/cm^{-1} 3475, 3230, 2240, 1740, 1710, 1580 and 1270; δ_H 1.6 and 2.0 (3 H, s, Me), 3.4 and 3.8 (3 H, s, CO_2Me), 4.5 and 4.6 (1 H, d, *J* 11, CH), 5.4 and 5.6 (1 H, d, *J* 11, CH), 6.2 and 6.5 (2 H, s, NH_2, D_2O-exch.), 7.6–7.8 (2 H, m, Ar) and 9.2 and 9.6 (1 H, s, NH, D_2O-exch.) (Found: C, 43.0; H, 3.4; N, 14.1. $C_{14}H_{13}Cl_3N_4O_3$ requires C, 42.9; H, 3.3; N, 14.3%).

Ethyl 2-(2,3,6-trichloro-α-cyanobenzyl)acetoacetate aminocarbonylhydrazone **3q**. M.p. 178–180 °C (decomp.); ν_{max}/cm^{-1} 3460, 3205, 2240, 1740, 1712, 1590 and 1230; δ_H 0.9 (3 H, t, *J* 7, CO_2CH_2Me), 2.0 (3 H, s, Me), 3.8 (2 H, q, *J* 7, CO_2CH_2Me), 4.5 (1 H, d, *J* 11, CH), 5.6 (1 H, d, *J* 11, CH), 6.5 (2 H, s, NH_2, D_2O-exch.) 7.6–7.8 (2 H, m, Ar), and 9.6 (1 H, s, NH, D_2O-exch.) (Found: C, 44.5; H, 3.6; N, 13.9. $C_{15}H_{15}Cl_3N_4O_3$ requires C, 44.4; H, 3.7; N, 13.8%).

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