mp 238 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 0.98 (s, 3 H), 1.67 (s, 9 H), 2.40 (s, 3 H), 2.72 (s, 3 H); MS calcd for $C_{22}H_{27}N_3OS$, m/z 381.1875 (HCl elim), found 381.1894; m/z (rel int) 381 (7), 335 (16), 334 (28), 278 (30), 220 (10), 172 (14), 147 (29), 146 (32), 131 (12), 130 (22), 106 (10), 105 (100); IR 2900, 1640, 1535 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_3OSCl$: C, 63.23; H, 6.71; N, 10.06; S, 7.66. Found: C, 62.84; H, 6.83; N, 9.77; S, 7.31.

1-Benzyl-4-(*tert*-butylimino)-5-hydroxy-2-(methylthio)-5-phenyl-2-imidazoline hydrochloride (14n): mp 169 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 1.51 (s, 9 H), 2.72 (s, 3 H), 4.27, 4.40 (AB syst, J = 16 Hz, 2 H), 9.12 (br, 1 H), 10.57 (br, 1 H); MS calcd for $C_{21}H_{25}N_3OS$, m/z 367.1718 (HCl elim), found 367.1704; m/z (rel int) 367 (2), 292 (18), 276 (10), 220 (27), 105 (82), 104 (12), 91 (100). Anal. Calcd for $C_{21}H_{26}N_3OSCl$: C, 62.45; H, 6.44; N, 10.40; S, 7.93; Cl, 8.79. Found: C, 61.93; H, 6.48; N, 10.33; S, 7.76; Cl, 8.97.

4-(*tert*-Butylimino)-5-hydroxy-2-(methylthio)-5-phenyl-1-isopropyl-2-imidazoline hydrochloride (14o): mp 220 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 1.05 (d, J = 7 Hz, 3 H), 1.27 (d, 3 H), 1.51 (s, 9 H), 2.88 (s, 3 H), 3.87 (m, 1 H), 7.44 (s, 5 H), 8.87 (br, 1 H), 10.10 (br, 1 H); MS calcd for $C_{17}H_{25}N_3S$, m/z 303.1769 [HCl elim and $(M - O)^{\cdot+}$], found 303.1770; m/z (rel int) 303 (4), 272 (12), 174 (18), 166 (11), 158 (17), 146 (9), 110 (53), 105 (100); IR 2900, 1640, 1541 cm^{-1}. Anal. Calcd for $C_{17}H_{26}N_3OSCl$: C, 57.38; H, 7.31; N, 11.81; S, 9.00; Cl, 9.99. Found: C, 57.25; H, 7.49; N, 11.61; S, 8.76; Cl, 10.46.

1-*tert*-Butyl-4-(*tert*-butylimino)-5-hydroxy-2-(methylthio)-5-phenyl-2-imidazoline hydrochloride (14p): mp 218 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 1.45 (s, 18 H), 2.90 (s, 3 H), 7.45 (br, 5 H), 8.97 (br, 1 H), 9.22 (s, 1 H). Anal. Calcd for $C_{18}H_{28}N_3OSCl$: C, 58.45; H, 7.57; N, 11.36; S, 8.66; Cl, 9.60. Found: C, 58.66; H, 7.61; N, 11.14; S, 8.78; Cl, 9.68.

Preparation of 2-Thioxodiazolidines 19a,b. By a similar procedure, an equimolar mixture of imidoyl chloride **1c** (10 mmol) and ketimine **17a** (2.2 g) or **17b** (1.6 g) was treated with 2 equiv of isopropyl isocyanide **3b** (1.4 g) in $CHCl_3$ (5 mL) at rt for 3 or 5 d (method A). Workup of the brownish solution in the usual way gave a crystalline compound which was triturated with MeOH and collected by filtration. MeCl elimination was observed when the reaction was carried out in $CDCl_3$ and analyzed by ^1H NMR.

1,3-Diisopropyl-5,5-diphenyl-4-(isopropylimino)-2-thioxo-1,3-diazolidine (19a): mp 189 °C (from MeOH) (56% yield); ^1H NMR δ 0.46 (d, J = 7 Hz, 6 H), 1.15 (d, 6 H), 1.51 (d, 6 H), 3.35 (m, 1 H), 3.65 (m, 1 H), 5.42 (m, 1 H); ^{13}C NMR δ 18.4, 19.6, 22.9 (3 qm, ^1J = 127 Hz, CH_3), 47.3, 48.9, 49.1 (3 dm, ^1J = 137 Hz, $CHMe_2$), 74.6 (m, C-5), 135.2 (t, ^3J = 7 Hz, 2 quat arom C), 128.6, 129.1, 128.7 (2 dt and dd, ^1J = 160 Hz, other arom C), 152.8 (t, ^3J = 6 Hz, C-4), 178.5 (dd, ^3J = 5 Hz, C-2); MS calcd for $C_{24}H_{31}N_3S$, m/z 393.2239 ($M^{\cdot+}$), found 393.2264; m/z (rel int) 393 (14), 236 (11), 235 (63), 224 (21), 194 (18), 193 (100), 165 (28); IR 1673 cm^{-1}. Anal. Calcd for $C_{24}H_{31}N_3S$: C, 73.28; H, 7.89; N, 10.69; S, 8.14. Found: C, 73.38; H, 8.03; N, 11.13; S, 7.70.

1,3-Diisopropyl-5-methyl-5-phenyl-4-(isopropylimino)-2-thioxo-1,3-diazolidine (19b): mp 129 °C (MeOH) (54% yield); ^1H NMR δ 0.45 (d, J = 7 Hz, 3 H), 0.97 (d, 3 H), 1.17 (d, 3 H), 1.50 (d, 3 H), 1.47 (d, 6 H), 1.82 (s, 3 H), 3.30 (m, 1 H), 3.51 (m, 1 H), 5.36 (m, 1 H), 7.30 (s, 5 H); IR 1665 cm^{-1}. Anal. Calcd for $C_{19}H_{29}N_3S$: C, 68.88; H, 8.76; N, 12.69; S, 9.67. Found: C, 68.59; H, 8.91; N, 12.41; S, 9.49.

Registry No. **1a**, 94518-64-6; **1b**, 94518-63-5; **1c**, 94518-60-2; **1d**, 138877-64-2; **1e**, 90496-26-7; **2a**, 622-29-7; **2b**, 6852-54-6; **2c**, 3096-95-5; **2d**, 780-25-6; **2e**, 6852-56-8; **2f**, 6852-58-0; **3a**, 2769-71-3; **3b**, 598-45-8; **3c**, 2999-46-4; **3d**, 7188-38-7; **5a**, 138877-65-3; **5b**, 138877-66-4; **5c**, 138877-67-5; **5d**, 138877-68-6; **5e**, 138877-69-7; **5f**, 138877-70-0; **5g**, 138877-71-1; **5h**, 138877-72-2; **5i**, 138877-73-3; **5j**, 138877-74-4; **5k**, 138877-75-5; **5l**, 138877-76-6; **5m**, 138877-77-7; **5n**, 138898-83-6; **5o**, 138898-84-7; **9d**, 138877-78-8; **9e**, 138877-79-9; **9h**, 138877-80-2; **10**, 138877-81-3; **12**, 138877-82-4; **13n**, 138877-83-5; **13p**, 138877-84-6; **14k**, 138877-85-7; **14l**, 138877-86-8; **14m**, 138877-87-9; **14n**, 138877-88-0; **14o**, 138877-89-1; **14p**, 138877-90-4; **15a**, 25105-60-6; **15b**, 74119-36-1; **16a**, 138877-91-5; **16b**, 138877-92-6; **17a**, 27126-12-1; **17b**, 6907-73-9; **19a**, 138877-93-7; **19b**, 138877-94-8.

Supplementary Material Available: X-ray data for **14k** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Azide Ring-Opening–Ring-Closure Reactions and Tele-substitutions in Vicinal Azidopyrazole-, Pyrrole- and Indolecarboxaldehydes

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5-Chloro-1-methylpyrazole-4-carboxaldehydes **1** react with excess sodium azide in dimethyl sulfoxide to produce a mixture of 1-azidomethyl-4-cyanopyrazoles **2** and 4-cyano-5-hydroxy-1-methylpyrazoles **3**. Application of this reaction to the corresponding 5-chloro-1-phenylpyrazole-4-carboxaldehydes **5** gave 4-cyano-5-hydroxy-1-phenyl-pyrazoles **7** as the sole products in high yields. Likewise, 2-aryl-5-chloro-1-methylpyrrole-3,4-dicarboxaldehydes **9** rearranged to 2-aryl-4-cyano-5-hydroxy-1-methylpyrrole-3-carboxaldehydes **10** in high yields. In the indole series, treatment of 1-aryl-2-chloroindole-3-carboxaldehydes **11** with NaN_3 yielded a mixture of 1-aryl-3-cyano-2(3*H*)-indolones **13** and 1-aryl-5-azido-3-cyanoindoles **12**, both products resulting from a ring-opening–ring-closure reaction with concomitant nucleophilic tele-substitution at the 5-position of the indole ring.

We have previously[1,2] demonstrated that many vicinal chloro heteroaryl carboxaldehydes react with azide anion to yield the corresponding vicinal heteroarylcarboxaldehydes in fair yields if the reaction is carried out below 60 °C. At slightly higher temperatures, however, many heterocyclic azides are labile and undergo ring opening with concomitant rearrangement.[3] In two recent com-

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Scheme I. Rearrangement of 5-Chloro-1-methylpyrazole-4-carboxaldehydes

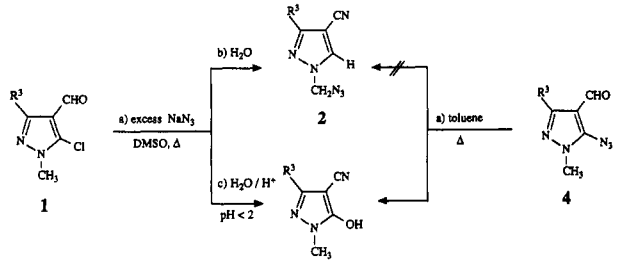


Table I

starting compd	R^3	yield (%) of 2	yield (%) of 3
1a	H	20	not isolated[a]
1b	CH_3	29	not isolated
1c	C_6H_5	23	60
1d	4-ClC_6H_4	23	69
1e	4-$CH_3OC_6H_4$	16	70

[a] Alternatively, pyrolysis of 5-azido-1-methylpyrazole-4-carboxaldehyde[2] in toluene gave **3a** in 56% yield (Table II). For tautomerism of **3** shown here in the hydroxy form, see later.

Table II

starting compd	R^3	yield (%) of 7
6a	CH_3	46[a] (7a)
5b	C_6H_5	71[b] (7b)
6c	$CH(CH_3)_2$	14[a] (7c)
6d	$C(CH_3)_3$	27[a] (7d)

[a] The 5-azidopyrazole was heated in toluene. [b] A one-pot reaction directly from the 5-chloropyrazole.

munications we reported[4,5] ring-opening–ring-closure reactions in the pyrazole and indole series. We had anticipated that this rearrangement was general and should be useful in the synthesis of new pyrazoles and indoles. We now report a full account of this reaction in the pyrazole, indole, and pyrrole series.

Results

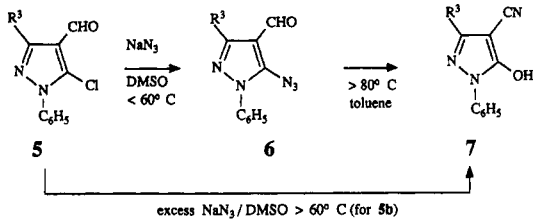
Rearrangements. i. Pyrazoles. Scheme I shows the results when a series of 5-chloro-1-methylpyrazole-4-carboxaldehydes **1** were heated with excess (3 mol) sodium azide in DMSO at 80–110 °C. The progress of the reaction was monitored by the evolution of N_2. After 1 equiv of N_2 was collected the reaction was quenched immediately by addition of ice–water. The crystalline 1-(azidomethyl)-4-cyanopyrazoles **2** were characterized by spectral and analytical data. We have reported an X-ray crystal structure for **2b**.[4] After isolation of neutral compounds **2**, the remaining aqueous phase was acidified (HCl 4 M) to pH 2 to precipitate the main products, 4-cyano-1-methyl-5-hydroxypyrazoles **3**. The structure of new 4-cyano-5-hydroxypyrazoles **3** and **7** is based on analytical and spectroscopic data. Compounds **3c**, **7a**, and **7b** are known,[6-8] having been prepared previously by completely different routes. Products **2** and **3** were easily separated and obtained in 70–83% total yields after recrystallization.

In all cases, the 3-aryl-5-azido-1-methylpyrazole-4-carboxaldehyde is formed as the primary product before rearrangement takes place (Figure 1). Excess azide ion causes tele-substitution to take place at the 1-methyl group because the heating 5-azido-1-methylpyrazole-4-carboxaldehyde[2] in toluene yielded 4-cyano-5-hydroxy-1-methylpyrazole (**3a**, 56%) as the sole product (TLC).

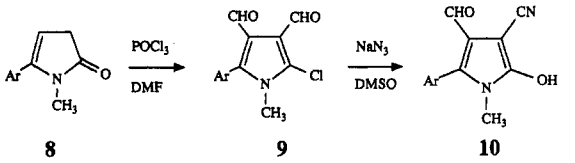
For azidopyrazoles **6** carrying a phenyl group at the ring nitrogen (N-1) a tele-substitution is not possible, and 4-cyano-5-hydroxypyrazoles **7** are the only products isolated (14–71%).

These reactions were carried out either by a one-pot reaction (**5b**) or in a two-step process in which the 5-azidopyrazole (**6a,c,d**) was first isolated and subsequently pyrolyzed (Scheme II). Synthetically, the one-pot reaction

Scheme II



Scheme III. Rearrangement of 2-Aryl-5-chloro-1-methylpyrrole-3,4-dicarboxaldehydes 9



Scheme IV. Rearrangement of 2-Chloroindole-3-carboxaldehydes

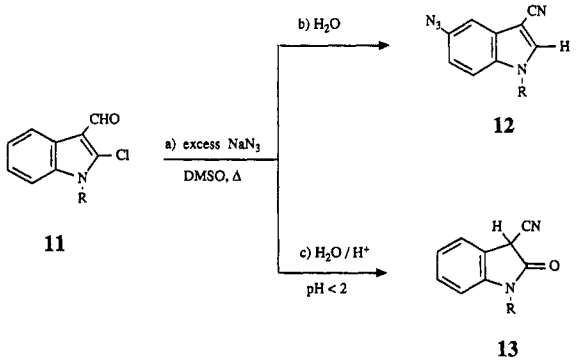


Table III

starting material	Ar	yield of 10 (%)
9a	C_6H_5	77 (10a)
9b	4-$CH_3C_6H_4$	90 (10b)

Table IV

starting compd	R	yield (%) of 12	yield (%) of 13
11a	CH_3	51 (12a)	40 (13a)
11b	C_6H_5	34 (12b)	25 (13b)
11c	$(CH_2)_3CH{=}CH_2$	24 (12c)	43 (13c)
11d	$CH_2C_6H_4$	14 (12d)	a

[a] Polymerization.

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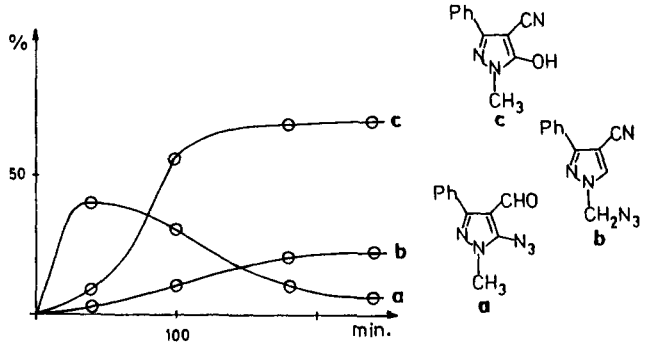
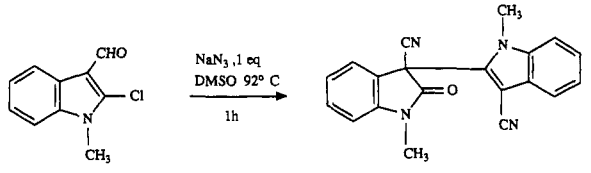


Figure 1. Rearrangement of 1c in DMSO-d_6 using the standard reaction conditions at 95 °C (see Experimental Section). Progress of the reaction was monitored by ^{1}H NMR (60 MHz), following the methylene and methyl protons.

Scheme V



11a 15

is preferable as it avoids isolation of the vicinal azidoaldehydes **6**.

ii. Pyrroles. In order to test this rearrangement in the pyrrole system, vicinal chloropyrrolecarboxaldehydes **9** were prepared by chloroformylation of arylpyrrol-5-ones **8**. Under reaction conditions identical to the one-pot reaction previously described, **9** rearranged smoothly upon treatment with azide in hot DMSO to yield 4-cyano-5-hydroxypyrroles **10** in yields of 77–90% (Scheme III).

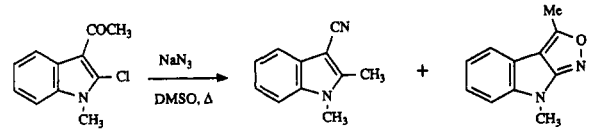
iii. Indoles. In the indole series the azide rearrangement reaction[5] was significantly faster than in the other two heterocycles. Reaction of 2-chloro-1-methylindole-3-carboxaldehydes **11a**[9] with excess sodium azide in DMSO at 97–100 °C for ≤5 min resulted in the evolution of 1 equiv of N_2. Immediate quenching with water gave 5-azido-3-cyano-1-methylindole (**12a**, 51%), whose structure was confirmed by X-ray crystal analysis.[5] Adjustment of the pH to 2 with HCl produced 3-cyano-1-methyl-2-(3*H*)-indolone (**13a**), bringing the total yield calculated from **11a** to 91%. The indolones **13** are new compounds and were characterized by analytical and spectral data.

Dimer Formation. In the indole series, TLC of the crude reaction mixtures in most cases revealed a number of minor products besides the two main products; the byproducts appeared after a few minutes of heating.

In order to investigate the result of prolonged heating, equimolar amounts of NaN_3 and 2-chloro-1-methylindole-3-carboxaldehyde (**11a**) were heated for 1 h at 92 °C in DMSO-d_6. The resulting dark reaction mixture contained only one product (**15**) according to TLC (Scheme V).

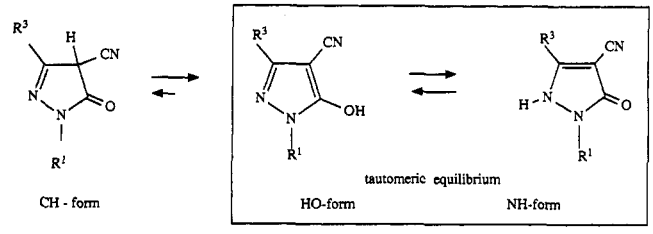
The mass spectrum of **15** showed m/z = 326 (M^+, 100) as the base peak, indicating a dimeric product. An IR absorption due to an indolone C=O was seen at 1727 cm^{-1} (3-cyano-1-methyl-2(3*H*)-indolone has C=O at 1729 cm^{-1}). The ^{1}H NMR shift values of the two methyl groups are close together and resemble the shifts found for 3-cyano-1-methyl-2(1*H*)-indolone. Furthermore, the ^{13}C NMR spectrum confirmed the presence of one CO, two NCH_3, and two CN groups. Preparation of the parent dimer has been reported by deDiesbach and Wiederkehr.[10]

Scheme VI

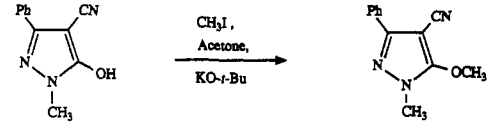


16 17 18

Scheme VII



Scheme VIII



3c 19

Table V

compd	UV (EtOH) λ_{max} (log ϵ)
3c	206 (4.34), 252 (4.05)
19	206 (4.26), 251 (3.89)

The formation of dimer **15** can be rationalized as a reaction between the indolone product **13** and the ring-closed 1-methyl-3-cyanoindole which may be formed during the reaction; alternatively, the dimer could be formed from two molecules of 3-cyano-2(3*H*)-indolone or its anion.

Azide Rearrangement in 3-Acetylindoles. The 3-keto group in an indole such as 3-acetyl-2-chloro-1-methylindole (**16**) is less reactive toward nucleophiles, compared to a 3-carboxaldehyde group in a similar indole. The azide rearrangement of 3-acetylindole **16** required heating to 120 °C, and consequently extensive decomposition was observed. A low yield of a product characterized as the 1,2-oxazoloindole **18** was isolated along with a main rearrangement product, the known[11] 3-cyano-1,2-dimethylindole (**17**); no tele-substitution product was observed in this reaction.

Tautomerism of Pyrazoles. The tautomeric equilibria of 1-substituted pyrazol-5-ones are complicated and have been studied intensely.[12] Substituents at C-4 decrease the "CH-form", while an electronegative group, such as CN, favors the "OH-form". Maquestiau et al.[13] have found that the IR-spectra of **7a** shows no CH-form in any solvent, while the NH-form is observed in polar solvents and the OH-form prevails in less polar solvents.

This propensity toward the OH-form is probably also seen here as all C-5 shifts in the ^{13}C-NMR of the present series of 4-cyanopyrazoles were in the range 156.9–158.2

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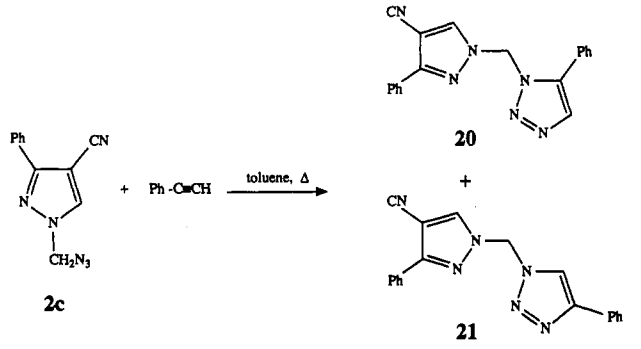
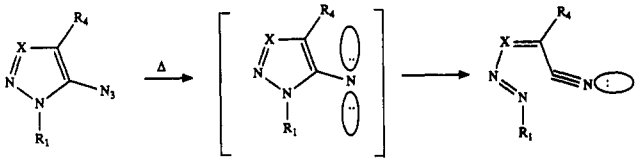
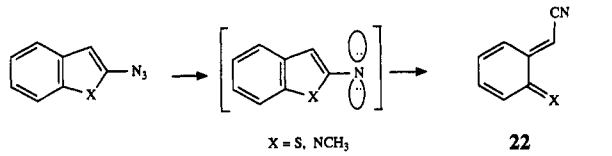
Scheme IX



Scheme X



Scheme XI



ppm. Freyer et al.[14] previously assigned δ 155 ppm to C-5 for the hydroxy tautomer of 3-methyl-5-hydroxy-1-phenylpyrazole. Methylation of **3c** gave the 5-methoxypyrazole **19**; the CH_3O protons are found at 4.33 ppm and the C-5 carbon at 157.5 ppm. Furthermore, **3c** and the corresponding 3-methoxypyrazole **19** showed similar UV spectra, suggesting similar π-systems (Table V).

Cycloaddition Reactions. The 1-azidomethyl group in the new pyrazoles **2** was expected[15,16] to show typical [3 + 2] cycloaddition reactions with an alkyne. For example, when 1-(azidomethyl)-4-cyano-3-phenylpyrazole (**2c**) was heated with an excess of phenylacetylene in toluene, a mixture of triazoles **20** and **21** (ratio 3:1 by ^1H NMR, total yield 91%) was isolated. The isomers were separated by fractional crystallization.

Discussion

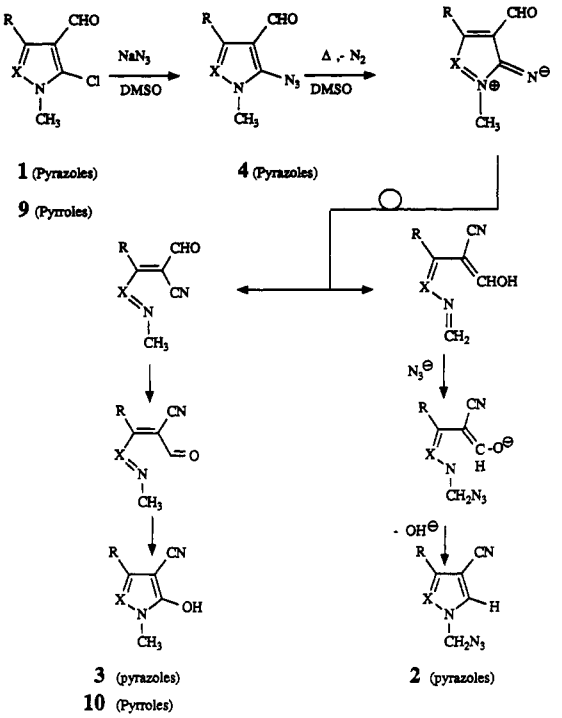
Thermally induced ring openings of five-membered heterocyclic azides are well-known[3] in the triazole (X = N) and the pyrazole series (X = CR_3). These reactions all follow Scheme X.

Related ring-opening reactions have been reported in thiophenes,[17] benzothiophenes,[18] and indoles.[19] Foresti et al.[20] have recently reported related ring openings in the 2-azidobenzo[*b*]thiophene and the 2-azidoindole series. In both cases the ring opening occurs via the ortho-quinoidal intermediate **22** which was intercepted with various dienophiles.

In the rearrangements described in this paper the primary step in each case is the formation of the vicinal azidoformyl heteroarenecarboxaldehyde. The rearrangement of pyrazole **1c** in DMSO-d_6 could be monitored by ^1H NMR (Figure 1).

This result clearly shows that the 5-azidopyrazole-4-carboxaldehyde a (**4c**) is formed as the primary product and that the ratio of rearrangement products a and b is relatively constant once the initial reaction is finished.

Reaction 1 shows a likely explanation for the formation of the two products formed in the pyrazole series. The excess of nucleophilic azide anion results in substitution at the 1-CH_3 group followed by ring closure to the azidomethylpyrazole **2**, while **3** is formed via an alternative route. Formation of **3** by pyrolysis of **3** in dry toluene can also be rationalized by this mechanism, and the same reaction scheme can be used to explain ring opening–ring closure in the pyrrole series.



Recently[21] we have isolated a ring-opened intermediate in a related azide ring opening of a pyrazole. This result supports a rearrangement taking place via an acyclic intermediate azo compound.

Reaction 2 shows a likely mechanism for the indole rearrangement. The reaction in the indole series is very fast, and it is evident that the intermediates correspond to those suggested in reaction 1. In the indole series, however, tele-substitution[5] occurs at the activated C-5 position.

The rearrangement of 2-azidoindole-3-carboxaldehydes is likely to involve an ortho-quinoidal intermediate, and in one case we tried to intercept it via an intramolecular Diels–Alder reaction. However, we were unable to detect any cycloaddition product in the rearrangement of 1-(penten-5-yl)indole **11c**.

5-Azidoindoles have recently been used for photoaffinity labeling studies in plants.[22] The synthetic route described in the present paper is an alternative to the classical me-

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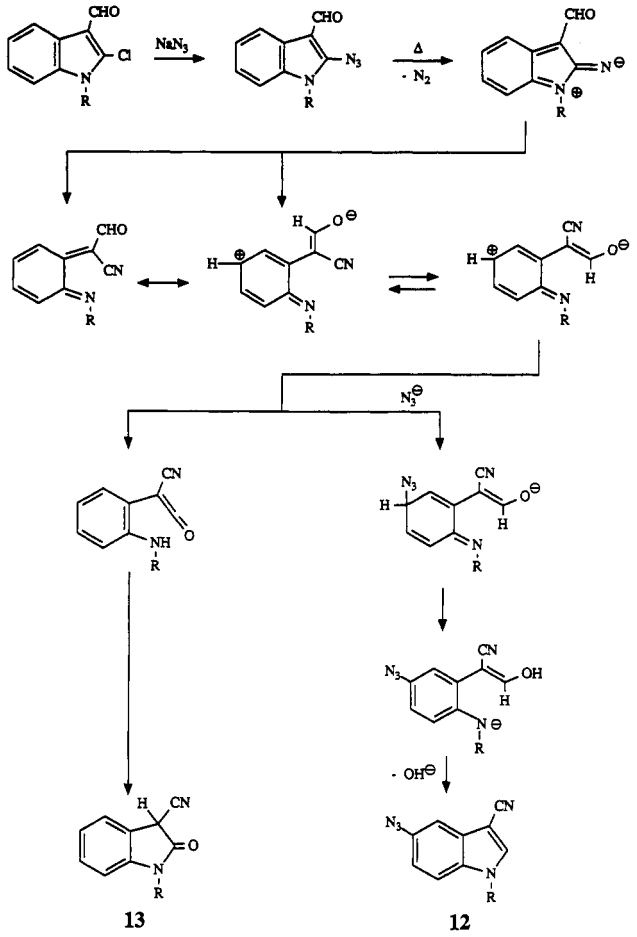

13 12

thod for preparing 5-azidoindoles. Furthermore, heterocyclic azides can usually be reduced to the corresponding amines, and when 5-azido-1-methylindole-3-carboxaldehyde (**12a**) was reduced using Soai et al.'s method[23] a 97% yield of 5-amino-3-cyano-1-methylindole (**24**) was obtained.

Experimental Section

General Methods. All melting points are uncorrected. Microanalyses were carried out by NOVO A/S Bagsvaerd, Denmark, or by Preben Hansen, University of Copenhagen.

Materials. The following compounds were prepared by literature methods: **1b** and **5b**,[24,25] 2-chloroindole-3-carboxaldehydes **11a,b,d**,[9,26,27] and vicinal azidopyrazolecarboxaldehydes **6a** and **6d**.[1,28]

i. Pyrazoles. Preparation of 5-Chloropyrazole-4-carboxaldehydes (1a–j), General Procedure. The chloroformylation (Vilsmeier–Haack) reagent was prepared by slow addition of $POCl_3$ (6.41 mL, 0.07 mol) to DMF (2.32 mL, 0.03 mol) under stirring and external cooling (maintaining the temperature <10 °C). The appropriate pyrazolone (10 mmol) was then added in one portion with stirring, and the reaction mixture was refluxed for 0.5–1 h. Progress of the reaction was monitored by TLC, when the starting material was consumed the dark colored reaction mixture was added either slowly to aqueous Na_2CO_3 (50%, 100 mL, 0 °C) or directly with stirring to ice-cold water (100 mL). If the product did not crystallize immediately, the aqueous phase

Scheme XII

12a **24**

was carefully neutralized (pH = 6–7, 3 mL 20% NaOH) and extracted with methylene chloride. The organic phase was dried (Na_2SO_4), filtered, and concentrated in vacuo. The aqueous phase may alternatively be extracted with ether ("Kutcher–Steudel"-extractor).

5-Chloro-1-methylpyrazole-4-carboxaldehyde (1a): yield 72%, mp 50–51 °C, colorless crystals (petroleum ether, bp 60–70 °C); IR (KBr) 1675, 1526 cm^{-1}; MS (*m/z*) 146 (M^+ + 2, 18), 145 (M^+ + 1, 34), 144 (M^+, 58), 143 (M^+ – 1, 100), 115 (2), 28 (21); ^1H NMR ($CDCl_3$) δ 9.81 (1 H, s, CHO), 7.96 (1 H, s, H3), 3.93 (3 H, s, Me); ^{13}C NMR ($CDCl_3$) δ 182.2 (CHO), 139.7 (C-3), 132 (C-5), 119 (C-4), 36.14 (CH_3). Anal. Calcd for $C_5H_5N_2ClO$: C, 41.54; H, 3.49; N, 19.38. Found: C, 41.33; H, 3.42; N, 18.87.

5-Chloro-1-methyl-3-phenylpyrazole-4-carboxaldehyde (1c): yield 80%, mp 61–62 °C (EtOH) (lit.[29,30] mp 63 °C); IR (KBr) 1665 (CO), 1500 cm^{-1} (C_3=N); MS (*m/z*) 222 (M^+ + 2, 33), 221 (M^+ + 1, 41), 220 (M^+, 100), 219 (M^+ – 1, 86), 192 (6), 185 (8), 77 (17); ^1H NMR ($CDCl_3$) δ 9.93 (s, 1 H, CHO), 7.70–7.40 (m, 5 H, aryl), 3.90 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 183.0 (CHO), 130.7 (C-4), 153.1 (C-3), 115.3 (C-4), 36.1 (CH_3), C_{aryl}: 129.1, 128.5, 128.3. Anal. Calcd for $C_{11}H_9N_2ClO$: C, 59.86; H, 4.33; N, 12.70. Found: C, 60.04; H, 4.14; N, 12.57.

5-Chloro-3-(4-chlorophenyl)-1-methylpyrazole-4-carboxaldehyde (1d): yield 77%, mp 82–83 °C (EtOH); IR (KBr) 1680 cm^{-1} (CO); MS (*m/z*) 258 (M^+ + 4, 10), 257 (M^+ + 3, 15), 256 (M^+ + 2, 63), 255 (M^+ + 1, 57), 254 (M^+, 100), 253 (M^+ – 1, 71), 219 (38); ^1H NMR ($CDCl_3$) δ 9.93 (s, 1 H, CHO), 7.83 (d, 2 H, *J* = 9 Hz), 7.43 (d, 2 H, *J* = 9 Hz), 3.93 (s, 3 H, CH_3). Anal. Cacld for $C_{11}H_8N_2ClO$: C, 51.79; H, 3.16; N, 10.98; Cl, 27.79. Found: C, 52.26; H, 3.17; N, 10.80; Cl, 27.50.

5-Chloro-3-(4-methoxyphenyl)-1-methylpyrazole-4-carboxaldehyde (1e): yield 82%, mp 79–80 °C (EtOH); IR (KBr) 1682 cm^{-1} (CO); MS (*m/z*) 252 (M^+ + 2, 32), 251 (M^+ + 1, 21), 250 (M^+, 100), 249 (M^+ – 1, 28), 235 (16), 219 (19), 207 (43), 77 (53); ^1H NMR ($CDCl_3$) δ 9.93 (s, 1 H, CHO), 7.76 (d, 2 H, *J* = 9 Hz), 6.97 (d, 2 H, *J* = 9 Hz), 3.90 (s, 3 H, CH_3O), 3.86 (s, 3 H, CH_3). Anal. Calcd for $C_{12}H_{11}N_2ClO_2$: C, 57.49; H, 4.42; N, 11.17; Cl, 14.14. Found: C, 57.24; H, 4.42; N, 11.06; Cl, 14.18.

5-Chloro-3-isopropyl-1-phenylpyrazole-4-carboxaldehyde (5c): yield 87%, mp 47–48 °C (aq EtOH); IR (KBr) 1682 cm^{-1} (CO); MS (*m/z*) 250 (M^+ + 2, 27), 248 (M^+, 83), 233 (43), 77 (100); ^1H NMR ($CDCl_3$) δ 10.00 (s, 1 H, CHO), 7.70–7.30 (m, 5 H, C_6H_5), 3.50 (h, 1 H, *J* = 7 Hz, CH), 1.35 (d, 6 H, *J* = 7 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 183.6 (CHO), 160.7 (C-3), 133.9 (C-5), 116.2 (C-4), 27.76 (CH), 21.09 (CH_3), C_{aryl}: 137.2, 129.2, 129.0, 125.3. Anal. Calcd for $C_{13}H_{13}N_2ClO{\cdot}0.25\ H_2O$: C, 61.66; H, 5.37; N, 11.06. Found: C, 61.74; H, 5.33, N, 11.07.

5-Azido-3-isopropyl-1-phenylpyrazole-4-carboxaldehyde (6c). 5-Chloro-3-isopropyl-1-phenylpyrazole-4-carboxaldehyde (**5c**) (3.0 g, 12 mmol) and NaN_3 (2.36 g, 36 mmol) were dissolved in DMSO, and the mixture was stirred for 1 h at 70 °C. The mixture was cooled to rt and added to H_2O (0 °C, 200 mL). The precipitated azidoaldehyde (**6c**) was almost analytically pure: yield 2.95 g (95%), mp 73–74 °C (aq EtOH); IR (KBr) 2157 (N_3), 1656 (CHO) cm^{-1}; MS (*m/z*) 255 (M^+, 11), 227 (11), 105 (19), 77 (100), 51 (12); ^1H NMR ($CDCl_3$) δ 10.01 (s, 1 H, CHO), 7.70–7.40 (m, 5 H, aryl), 3.40 (m, *J* = 7 Hz, 1 H, CH), 1.45 (d, *J* = 7 Hz, 6 H, CH_3). Anal. Calcd for $C_{13}H_{13}N_5O$: C, 61.17; H, 5.13; N, 27.43. Found: C, 61.07; H, 5.13; N, 27.29.

4-Cyano-1-(azidomethyl)pyrazoles. General One-Pot Procedure. The 5-chloro-3-substituted-1-methylpyrazole-4-

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carboxaldehyde (10 mmol) and NaN_3 (1.96 g, 30 mmol) were stirred in dry DMSO (20 mL). At 60 °C the 5-azidopyrazole was formed (TLC) whereas further heating >85 °C resulted in the evolution of N_2. Reaction progress was monitored by collection of the nitrogen in a measuring cylinder. After collection of 1 equiv of nitrogen (224 mL, 10 mmol) the reaction was quenched by addition to water (80 mL, 0–10 °C) with stirring. Workup from the basic aqueous phase was performed either directly by filtration of the precipitate or by extraction.

1-(Azidomethyl)-4-cyanopyrazole (2a). The general procedure was followed, and after heating the reaction mixture at 105 °C for 210 min, workup by continuous extraction (ether) and recrystallization (H_2O) yielded 20% of **2a**: mp 83–84 °C (water); IR (KBr) 2235, 2157, 2125, 2100 cm^{-1}; MS (*m/z*) 148 (M^+, 30), 106 (79), 93 (54), 66 (42), 28 (100); UV (EtOH) λ_{max} 214 (3.85); ^1H NMR ($CDCl_3$) δ 8.05 (1 H, s, H3), 7.91 (1 H, s, H5), 5.42 (2 H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ 143.3 (C-3), 134.7 (C-5), 112.5 (CN), 93.8 (C-4), 65.4 (CH_2). Anal. Calcd for $C_5H_4N_6$: C, 40.54; H, 2.72; N, 56.73. Found: C, 40.53; H, 2.68; N, 56.59.

1-(Azidomethyl)-4-cyano-3-methylpyrazole (2b). Reaction conditions 100 °C for 210 min. The aqueous phase was extracted with chloroform, dried (Na_2SO_4), and evaporated in vacuo to yield 29% of **2b**: mp 70–71 °C (water); IR (KBr) 2232, 2153, 2122, 2083 cm^{-1}; MS (*m/z*) 162 (M^+, 42), 120 (100), 107 (28), 106 (63); peak match calcd 162.0654, found 162.0652; UV (EtOH) λ_{max} 215 (3.72), 229 (3.74); ^1H NMR ($CDCl_3$) δ 8.00 (1 H, s, H5), 5.40 (2 H, s, CH_2), 2.40 (3 H, s, Me); ^{13}C NMR ($CDCl_3$) δ 153.5 (C-3), 135.0 (C-5), 112.9 (CN), 93.5 (C-4), 65.2 (CH_2), 12.2 (CH_3). Anal. Calcd for $C_6H_6N_6$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.57; H, 3.73; N, 51.72.

1-(Azidomethyl)-4-cyano-3-phenylpyrazole (2c): reaction conditions 115 °C for 10 min, the product precipitated; yield 23%, mp 88–90 °C (EtOH/H_2O (2:3)); IR (KBr) 2240, 2168, 2130, 2100 cm^{-1}; MS (*m/z*) 224 (M^+, 76), 182 (25), 169 (100), 142 (42), 140 (61); UV (EtOH) λ_{max} 208 (4.29), 247 (4.14); ^1H NMR ($CDCl_3$) δ 8.09 (1 H, s, H5), 8.17–7.47 (5 H, m, C_6H_5), 5.43 (2 H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ 153.9 (C-3), 136.2 (C-5), 113.5 (CN), 91.2 (C-4), 65.6 (CH_2), C_{aryl}: 129.4 (C-4′), 128.66 (C-2′, C-6′), 126.46 (C-1′, C-3′, C-5′). Anal. Calcd for $C_{11}H_8N_6$: C, 58.92; H, 3.60; N, 37.48. Found: C, 58.63; H, 3.54; N, 37.18.

1-(Azidomethyl)-3-(4-chlorophenyl)-4-cyanopyrazole (2d): reaction conditions 95 °C for 5 h; yield 23%, mp 122–123 °C (EtOH); IR (KBr) 2235, 2122 cm^{-1}; MS (*m/z*) 260 (M^+ + 2, 22), 259 (M^+ + 1, 9), 258 (M^+, 76), 216 (16), 203 (100); ^1H NMR ($CDCl_3$) δ 8.10 (1 H, s, H5), 8.00 (2 H, d, *J* = 9 Hz), 7.50 (2 H, d, *J* = 9 Hz), 5.43 (2 H, s, CH_2). Anal. Calcd for $C_{11}H_7N_6Cl$: C, 51.07; H, 2.73; N, 32.49; Cl, 13.70. Found: C, 50.95; H, 2.69; N, 32.65; Cl, 13.48.

1-(Azidomethyl)-4-cyano-3-(4-methoxyphenyl)pyrazole (2e): reaction conditions 95 °C for 3 h, yield 16%, mp 96–97 °C (EtOH); IR (KBr) 2222, 2120 cm^{-1}; MS (*m/z*) 256 (M^+ + 2, 1), 255 (M^+ + 1, 18), 254 (M^+, 100), 212 (16), 199 (75); ^1H NMR ($CDCl_3$) δ 8.01 (1 H, s, H5), 7.98 (2 H, d, *J* = 9 Hz), 7.04 (2 H, d, *J* = 9 Hz), 5.40 (2 H, s, CH_2), 3.90 (3 H, s, Me). Anal. Calcd for $C_{12}H_{10}N_6O$: C, 56.68; H, 3.96; N, 33.05. Found: C, 56.42; H, 3.74; N, 33.17.

4-Cyano-5-hydroxypyrazoles. General One-Pot Method from the Vicinal Chloro Carboxaldehydes. The one-pot method, transforming the 5-chloro-1-methylpyrazole-4-carboxaldehyde (1), resulted in a slightly basic aqueous phase after isolation of the 1-(azidomethyl)pyrazole derivatives. When this aqueous phase was acidified with HCl (4 M) to pH 2, the 4-cyano-5-hydroxypyrazole precipitated readily. The product was isolated, washed with water, dried, and recrystallized.

4-Cyano-5-hydroxy-1-methyl-3-phenylpyrazole (3c): yield 60%, mp 233–234 °C (aq EtOH) (lit.[5] mp 225 °C); IR (KBr) 2945, 2221, 1620 cm^{-1}; MS (*m/z*) 200 (M^+ + 1, 13), 199 (M^+, 100), 198 (14), 171 (5), 128 (34), 77 (30), 51 (22); UV (EtOH) λ_{max} 206 (4.34), 252 (4.05); ^1H NMR (DMSO-d_6) δ 11.6 (1 H, s, exchanges D_2O), 8.00–7.38 (5 H, m, aryl), 3.70 (3 H, s, CH_3); ^{13}C NMR (DMSO-d_6) δ 157.1 (C-5), 148.3 (C-3), 115.0 (CN), 71.4 (C-4), 33.7 (CH_3) C_{aryl}: 131.3 (C-1′), 128.68 (C-2′, C-6′, C-4′), 125.44 (C-3′, C-5′). Anal. Calcd for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.33; H, 4.62; N, 21.17.

3-(4-Chlorophenyl)-4-cyano-5-hydroxy-1-methylpyrazole (3d): yield 47% (crude 69%), mp 208–210 °C (aq EtOH); IR (KBr) 2223, 1626 cm^{-1}; MS (*m/z*) 236 (M^+ + 3, 4), 235 (M^+ + 2, 34), 234 (M^+ + 1, 17), 233 (M^+, 100), 205 (7); ^1H NMR (DMSO-d_6) δ 9.50 (1 H, s, OH), 7.95 (2 H, d, *J* = 9 Hz), 7.60 (2 H, d, *J* = 9 Hz), 3.70 (3 H, s, CH_3). Anal. Calcd for $C_{11}H_8N_3ClO$: C, 56.55; H, 3.45; N, 17.98; Cl, 15.17. Found: C, 56.35; H, 3.53; N, 17.83; Cl, 15.30.

4-Cyano-5-hydroxy-3-(4-methoxyphenyl)-1-methylpyrazole (3e): yield 67% (crude 70%), mp 252–253 °C (MeOH); IR (KBr) 2220, 1618 cm^{-1}; MS (*m/z*) 230 (M + 1, 14), 229 (M^+, 100), 214 (20), 186 (8), 158 (4); ^1H NMR (DMSO-d_6) δ 7.76 (2 H, d, *J* = 9 Hz), 7.04 (2 H, d, *J* = 9 Hz), 6.75 (1 H, s, OH), 3.82 (3 H, s, OCH_3), 3.60 (3 H, s, NCH_3). Anal. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.72; H, 4.84; N, 18.09.

4-Cyano-5-hydroxypyrazoles. Pyrolysis of the Vicinal Azido Carboxaldehydes, General Method. The 5-azido-1-substituted-pyrazole-4-carboxaldehyde was dissolved in toluene (25 mL, 10 mmol) and the solution heated until all starting azide was consumed (TLC). The reaction mixture was then concentrated in vacuo to ca. half the volume and cooled, and the precipitated crystals were filtered.

4-Cyano-5-hydroxy-1-methylpyrazole (3a). 5-Azido-1-methylpyrazole-4-carboxaldehyde[2] (**1a**) (0.60 g, 3.97 mmol) was refluxed in toluene (15 mL) for 15 min, and the crystals which separated were isolated and recrystallized: yield 0.28 g (56%), mp 246–248 °C (EtOH/diisopropyl ether (4:1)); IR (KBr) 2450, 2222, 1636 cm^{-1}; MS (*m/z*) 123 (M^+, 100), 122 (10), 68 (29), 52 (36); UV (EtOH) λ_{max} 215 (3.84); ^1H NMR (CD_3OD) δ 7.65 (1 H, s, H3), 5.00 (1 H, s, OH), 3.62 (3 H, s, Me); ^{13}C NMR (CD_3OD) δ 158.2 (C-5), 141.1 (C-3), 114.5 (CN), 75.6 (C-4), 33.5 (CH_3). Anal. Calcd for $C_5H_5N_3O$: C, 48.78; H, 4.09; N, 34.13. Found: C, 48.93; H, 4.31; N, 33.21.

4-Cyano-5-hydroxy-3-methyl-1-phenylpyrazole (7a). 5-Azido-3-methyl-1-phenylpyrazole-4-carboxaldehyde (**6a**) (6.81 g, 0.030 mol) was heated (95 °C) in toluene (75 mL) for 3 h, the reaction mixture was then concentrated to ca. 40 mL and cooled, and the crystalline product was isolated (2.80 g, 46%): mp 217–218 °C (aq EtOH) (lit.[7] mp 218–220 °C); IR (KBr) 2860, 2227 cm^{-1}; MS (*m/z*) 199 (M^+, 100), 198 (29), 91 (38), 77 (29), 51 (15); ^1H NMR (DMSO-d_6) δ 11.5 (1 H, s, OH), 7.86–7.36 (5 H, m, C_6H_5), 2.28 (3 H, s, Me); ^{13}C NMR (DMSO-d_6) δ 156.9 (C-5), 150.0 (C-3), 114.1 (CN), 75.5 (C-4), 12.9 (CH_3), C_{aryl}: 136.9, 128.8, 126.4, 121.4. Anal. Calcd for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.58; H, 4.58; N, 21.20.

4-Cyano-5-hydroxy-1,3-diphenylpyrazole (7b). 5-Chloro-1,3-diphenylpyrazole-4-carboxaldehyde[25] (**5b**) (2.82 g, 0.0098 mol) and NaN_3 (1.95 g, 0.030 mol) was heated (95 °C) in DMSO (20 mL) for 150 min. After cooling, the reaction mixture was added to NaOH (80 mL, 0.5M) and the small amount of 5-azido-1,3-diphenylpyrazole-4-carboxaldehyde which precipitated was filtered off. Acidification with HCl (10 mL, 4 M) precipitated crystals of **7b**: yield 1.85 g (71%), mp 230–232 °C (EtOH); (lit.[8] mp 232–233 °C); IR (KBr) 3063, 2231 cm^{-1}; MS (*m/z*) 261 (M^+, 100), 260 (12), 91 (28), 77 (37), 51 (13). ^1H NMR (DMSO-d_6) δ 9.70 (1 H, s, OH), 8.13–7.36 (10 H, m, aryl); ^{13}C NMR (DMSO-d_6) δ 157.9 (C-5), 149.6 (C-3), 114.8 (CN), 73.1 (C-4), C_{aryl}: 137.1, 130.8, 129.0, 128.8, 128.6, 127.6, 126.9, 125.8, 122.0; UV (EtOH) λ_{max} 208 (4.32), 233 (4.32), 262 (4.25). Anal. Calcd for $C_{16}H_{11}N_3O$: C, 73.55; H, 4.24; N, 16.08. Found: C, 73.17; H, 4.22; N, 16.09.

4-Cyano-5-hydroxy-3-isopropyl-1-phenylpyrazole (7c). 5-Azido-3-isopropyl-1-phenylpyrazole-4-carboxaldehyde (**6c**) (1.0 g, 0.00392 mmol) in toluene (20 mL) was refluxed until an equivalent amount of N_2 was evolved (7 h). All of the starting aldehyde was consumed as seen by disappearance of the CHO peak in ^1H NMR or by TLC. Distillation in vacuo of toluene (ca. 10 mL) and storing overnight (5 °C) yielded crystals of **7c**, 0.116 g (14%): mp 173–175 °C (EtOH/H_2O); IR (KBr) 3435, 2220 cm^{-1}; MS (*m/z*) 228 (M^+, 13), 227 (84), 213 (14), 212 (100), 199 (14), 77 (31); ^1H NMR (DMSO-d_6) δ 8.70 (1 H, s, OH), 7.20–8.00 (5 H, m, C_6H_6), 3.00 (1 H, q, *J* = 7 Hz, CH), 1.27 (6 H, d, *J* = 7 Hz, CH_3); ^{13}C NMR (DMSO-d_6) δ 158.7 (C-3), 157.3 (C-5), 114.3 (CN), 73.3 (CN), 27.9 (C-4), 20.8 (CH_3), C_{aryl}: 137.2, 129.1, 126.7, 121.9. Anal. Calcd for $C_{13}H_{13}N_3O$, 0.125 H_2O: C, 68.04; H, 5.82; N, 18.31. Found: C, 68.14; H, 5.64; N, 17.82.

4-Cyano-5-hydroxy-3-*tert*-butyl-1-phenylpyrazole (7d). Prepared as described above from 5-azido-3-*tert*-butyl-1-phenylpyrazole-4-carboxaldehyde (**6d**) (1.92 g, 0.00713 mol) in

toluene (40 mL). Reflux for 4 h and concentration of the reaction mixture in vacuo gave **7d**: yield 0.53 g (27%), mp 154–156 °C (EtOH/H_2O); IR (KBr) 3436, 2225 cm^{-1}; MS (m/z) 241 (M^+, 100), 226 (38), 199 (9); ^1H NMR (DMSO-d_6) δ 9.90 (1 H, s, OH), 7.90–7.20 (5 H, m, C_6H_5), 1.40 (9 H, s, Me); ^{13}C NMR (DMSO-d_6) δ 160.4 (C-3), 157.8 (C-5), 115.1 (CN), 72.6 (C-4), 33.3 (C), 28.5 (CH_3), C_{aryl}: 137.4, 128.9, 126.7, 122.0. Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.42. Found: C, 69.33; H, 6.05; N, 17.26.

ii. Pyrroles. 2-Chloro-1-methyl-5-phenylpyrrole-3,4-dicarboxaldehyde (9a). 5-Hydroxy-1-methyl-5-phenylpyrrolidin-2-one (**8a**)[21,32] (9.55 g, 50 mmol) was refluxed (85 min) with a chloroformylation reagent prepared from DMF (11.6 mL) and $POCl_3$ (32 mL); the reaction mixture was then added to water (800 mL, 0 °C). Dropwise addition of NaOH (20%, 97 mL, with cooling) until pH = 5.5 gave brown crystals. This crude product was washed with water and recrystallized from aq EtOH to give **9a** 9.8 g (79%): mp 122–124 °C (aq EtOH); IR (KBr) 1678, 1616 cm^{-1}; MS (m/z) 247 (M^+, 66), 218 (100); ^1H NMR ($CDCl_3$) δ 10.43 (1 H, s, CHO), 9.73 (1 H, s, CHO), 7.63–7.47 (5 H, m, aryl), 3.51 (3 H, s, NCH_3); ^{13}C NMR ($CDCl_3$) δ 186.1 (CHO), 185.9 (CHO), 143.1 (C-2), 125.4 (C-5), 121.0 and 118.3 (C-3, C-4), 31.8 (CH_3), C_{aryl}: 130.58, 129.96 (C-4′), 128.69, 127.45 (C-1′). Anal. Calcd for $C_{13}H_{10}NClO_2$: C, 63.04; H, 4.07; N, 5.66. Found: C, 63.18; H, 4.16; N, 5.56.

2-Chloro-1-methyl-5-(4-methylphenyl)pyrrole-3,4-dicarboxaldehyde (9b). Prepared as described above from 5-hydroxy-1-methyl-5-(4-methylphenyl)pyrrolidin-2-one (**8b**)[6] (8.20 g, 40 mmol) by refluxing (20 min) with the chloroformylation reagent from DMF (10 mL) and $POCl_3$ (26 mL). The reaction mixture was then added to water (400 mL, 0 °C), followed by NaOH (20%, 75 mL) with cooling to pH = 6.5. Extraction with ether, washing with $NaHCO_3$ solution (50%), drying (Na_2SO_4), and concentration in vacuo followed by recrystallization of the crude product gave **9b**: yield 7.0 g (67%), mp 106–107 °C (EtOH); IR (KBr) 1672, 1494 cm^{-1}; MS (m/z) 261 (M^+, 82), 232 (100), 197 (26), 154 (22), 128 (24); ^1H NMR ($CDCl_3$) δ 10.45 (1 H, s, CHO), 9.73 (1 H, s, CHO), 7.35 (4 H, s, aryl), 3.52 (3 H, s, N-CH_3), 2.46 (3 H, s, CH_3); ^{13}C NMR 186.0 (CHO), 185.8 (CHO), 143.3 (C-5), 124.3 (C-2), 120.9 and 118.2 (C-3, C-4), 31.8 (CH_3), 21.3 (CH_3), C_{aryl}: 140.10 (C-4′), 130.35, 129.31, 125.19 (C-1′). Anal. Calcd for $C_{14}H_{12}NClO_2$: C, 64.25; H, 4.62; N, 5.35. Found: C, 64.14; H, 4.66; N, 5.15.

3-Cyano-2-hydroxy-1-methyl-5-phenylpyrrole-4-carboxaldehyde (10a). A mixture of 2-chloro-5-phenylpyrrole-3,4-dicarboxaldehyde (**9a**) (5.50 g, 22 mmol) and NaN_3 (5.00 g) in DMSO (50 mL) was heated with stirring (80 °C) for 50 min, and the reaction mixture was then added to water (250 mL, 0 °C). Acidification with HCl (4 M), extraction with ether, washing with saturated NaCl, drying (Na_2SO_4), and concentration in vacuo followed by recrystallization of the crude product gave **10a**, 3.85 of (76%): mp 182–184 °C dec (aq EtOH); IR (KBr) 2960, 2223, 1662 cm^{-1}; MS (m/z) 226 (M^+, 100), 225 (80); ^1H NMR (DMSO-d_6) δ 9.43 (1 H, s, CHO), 7.63 (5 H, s, C_6H_6), 5.30 (1 H, s, exchange D_2O), 3.36 (3 H, s, Me); ^{13}C NMR (DMSO-d_6) δ 183.1 (CHO), 153.6 (C-2), 127.0 (C-5), 118.4 (C-4), 115.3 (CN), 68.4 (C-3), 29.8 (CH_3), C_{aryl}: 137.1 (C-1′), 130.62, 128.49, 129.37 (C-4′); UV (EtOH) λ_{max} 206 (4.32), 231 (4.32), 312 (4.07). Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 68.76; H, 4.46; N, 12.18.

3-Cyano-2-hydroxy-1-methyl-5-(4-methylphenyl)pyrrole-4-carboxaldehyde (10b). Prepared as described above from 2-chloro-1-methyl-5-(4-methylphenyl)pyrrole-3,4-dicarboxaldehyde (**9b**) (5.22 g, 20 mmol) and NaN_3 (4.68 g) in DMSO (40 mL), heating at 75 °C for 110 min, addition to water (400 mL, 0 °C), and isolation of the precipitated crystals after acidification gave practically analytically pure **10b**, 4.3 g (90%): mp 225–226 °C dec (EtOH); IR (KBr) 2960, 2226, 1656 cm^{-1}; MS (m/z) 240 (M^+, 100), 239 (75), 225 (32), 211 (56), 132 (26); ^1H NMR (DMSO-d_6) δ 9.35 (1 H, s, CHO), 7.36 (4 H, s, C_6H_4), 5.30 (1 H, s, exchange D_2O), 3.30 (3 H, s, NCH_3), 2.39 (3 H, s, CH_3); ^{13}C NMR (DMSO-d_6), 183.0 (CHO), 153.7 (C-2), 124.1 (C-5), 118.2 (C-4), 115.4 (CN), 68.5 (C-3), 29.7 (CH_3), 20.4 (CH_3), C_{aryl}: 138.99 (C-1′), 137.82 (C-4′), 130.50, 129.04; UV (EtOH) λ_{max} 204 (4.26), 237 (4.16), 314 (4.14). Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.85; H, 5.05; N, 11.80

iii. Indoles. 5-Azido-3-cyano-1-methylindole (12a). 2-Chloro-1-methylindole-3-carboxaldehyde (**11a**)[9] (1.94 g, 10 mmol) was rapidly added to a mixture of NaN_3 (1.95 g, 30 mmol) and DMSO (30 mL) with stirring while the temperature was maintained at 97 °C. The temperature rose to 105 °C, and during 10 min the equivalent amount of N_2 (224 mL = 10 mmol) was evolved. The reaction mixture was rapidly cooled and added to water (90 mL, 0 °C), and the precipitated crystals of **12a** were isolated to give 1.0 g (51%): mp 134–135 °C (EtOH/pentane); IR (KBr) 2120, 2220 cm^{-1}; MS (m/z) 197 (M^+, 60), 168 (100); peak matching calcd 197.070 14, found 197.077 82; ^1H NMR ($CDCl_3$) δ 7.60 (1 H, s, H2), 7.50–6.90 (3 H, m, H-4, H-6, H-7), 3.90 (3 H, s, NMe); ^{13}C NMR ($CDCl_3$) δ 136.3 (C-2), 134.9 (C-7a), 133.5, 128.6 (C-3a and C-5), 115.9 (C-4), 115.1 (CN), 111.5 (C-7), 108.9 (C-6), 85.1 (C-3), 33.6 (CH_3). Anal. Calcd for $C_{10}H_7N_5$: C, 60.91; H, 3.58; N, 35.51. Found: C, 60.25; H, 3.45; N, 35.27. Compound **12a** is relatively unstable and light-sensitive, which is reflected in the carbon analysis. During recrystallization a fraction which was insoluble in pentane was also isolated yielding 0.1 g (6%) of the dimer **15**, mp 218–219 °C as described below.

3-Cyano-1-methyl-2(3*H*)-indolone (13a). The aqueous phase from which **12a** was isolated was acidified with HCl (4 M) to pH = 4. Extraction with $CHCl_3$, drying (Na_2SO_4), and concentration in vacuo followed by preparative layer chromatography (PTLC, SiO_2, CH_2Cl_2/MeOH (10:1)) gave **13a** 0.34 g (40%), mp 74–75 °C; IR (KBr) 2205, 1729 cm^{-1}; MS (m/z) (relative intensity 172 (M^+, 100), 157 (10), 143 (20), 117 (20), 103 (8); ^1H NMR (DMSO-d_6) δ 6.80–7.56 (4 H, m, H-4, H-5, H-6, H-7), 5.70 (1 H, bs, exchange D_2O), 3.26 (3 H, s, Me). Anal. Calcd for $C_{10}H_8N_2O$: C, 69.76; H, 4.68; N, 16.27. Found: C, 69.30; H, 4.66; N, 16.02.

3-Cyano-1-methyl-3-(3-cyano-1-methyl-2-indolyl)-2(3*H*)-indolone (15). 2-Chloro-1-methylindole-3-carboxaldehyde (**11a**)[9] (1.95 g, 10 mmol) was added to a mixture of NaN_3 (0.65 g, 10 mmol) and DMSO (30 mL) with stirring while the temperature was maintained at 92 °C. The temperature rose to 99 °C, and the reaction mixture was kept at 92 °C for 1 h. After cooling the dark red-brown reaction mixture was added to water (90 mL, 0 °C) and the dark brown crystals of **15** were filtered off, 0.55 g (34%): mp 218–219 °C (EtOH); IR (KBr) 2220, 1727 cm^{-1}; UV (abs EtOH) λ_{max} 285 (3.67), 225 (4.40); MS (m/z) 326 (M^+, 100), 311 (6), 297 (20), 282 (12), 268 (14); peak matching calcd 326.116 76, found 326.118 74; ^1H NMR ($CDCl_3$) δ 6.96–7.70 (8 H, m, aryl, 3.90 (3 H, s, CH_3), 3.33 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.5 (C2, CO), 149.1 (C-2′), 136.7 and 135.9 (C-7a′, C-7a), 127.7 and 127.6 (C-4a, C4a′), 130.8, 125.8, 125.3, 124.2, 122.5, 117.4, 116.8 (CN), 114.5 (CN), 111.4 and 109.4 (C-7 and C-7′), 85.8 (C-3), 51.6 (C-3′), 33.8 (CH_3), 27.3 (CH_3). Anal. Calcd for $C_{20}H_{14}N_4O$: C, 73.60; H, 4.32; N, 17.16. Found: C, 73.43; H, 4.25; N, 17.18.

2-Chloro-1-(4-pentenyl)indole-3-carboxaldehyde (11c). To a solution of 18-crown-6 0.75 g (Aldrich) in dry THF (50 mL) was added potassium *tert*-butoxide (3.75 g, 33.6 mmol), and 2-chloro-3-formylindole[33] (5.15 g, 28.6 mmol). After the solution was stirred for 15 min, 5-bromopentene (5.0 g, 33.6 mmol) in dry THF (20 mL) was slowly added. The reaction mixture was stirred (20 °C) for 44 h (all starting material consumed, TLC), and concentration in vacuo and Kugelrohr distillation afforded a pale yellow oil: yield 5.75 g (81%), oven temp 150 °C (0.001 mbar); IR (KBr) 1662 cm^{-1}; MS (m/z) 247 (M^+, 100), 218 (45), 212 (68), 192 (95), 158 (70); ^1H NMR ($CDCl_3$) δ 10.17 (1 H, s, CHO), 8.32–8.30 (1 H, m, H-4), 7.26–7.32 (3 H, m, H-5, H-7, H-6), 5.90–5.74 (1 H, m, H-4′), 5.13–5.05 (2 H, m, H-5′), 4.27–4.21 (2 H, t, H-1′), 2.20–2.12 (2 H, q, J = 3 Hz), 2.00–1.88 (2 H, q, J = 3 Hz); peak match calcd 247.0764, found 247.0764. Anal. Calcd for $C_{14}H_{14}NClO$: C, 67.87; H, 5.70; N, 5.65; Cl, 14.31. Found: C, 67.79; H, 5.71; N, 5.59; Cl, 14.45.

5-Azido-3-cyano-1-phenylindole (12b). This compound was prepared essentially as described above from 2-chloro-1-phenylindole-3-carboxaldehyde (**14b**)[26] (1.25 g, 5 mmol) and NaN_3 (0.97 g, 15 mmol) in DMSO (15 mL) at 92 °C. Stirring for 5 min at 108 °C gave 120 mL of N_2 (112 mL = 5 mmol); addition to water and isolation of the precipitate, drying and recrystallization gave **12b**: yield 0.45 g (34%), mp 169–170 °C (EtOH); IR (KBr) 2225,

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2108 cm^{-1}; MS (m/z) 259 (M^+, 16), 230 (100), 231 (75), 203 (6), 77 (32), 51 (26); ^1H NMR ($CDCl_3$) δ 7.87 (1 H, s, H-2), 7.43–7.66 (2 H, m, H-6, H-4), 6.93–7.19 (6 H, m, aryl, H-7). Anal. Calcd for $C_{15}H_9N_5$: C, 69.49; H, 3.50; N, 27.01. Found: C, 69.38; H, 3.49; N, 26.47.

5-Azido-3-cyano-1-(4-pentenyl)indole (12c). A mixture of 2-chloro-1-(4-pentenyl)indole-3-carboxaldehyde (**11c**) (2.48 g, 10 mmol) and NaN_3 (1.96 g, 30 mmol) in DMSO (15 mL) was stirred at 80–95 °C for 20 min. Addition of the reaction mixture to water (100 mL, 0 °C) and extraction with ether, drying ($NaSO_4$), and concentration in vacuo followed by chromatography (PTLC, SiO_2, ether/petroleum ether bp. 80 °C as eluent) yielded **12c** as the most unpolar fraction: oil, yield 0.30 g (24%); IR (neat), 2219 (CN), 2109 (N_3) cm^{-1}; MS (m/z) 251 (M^+, 50), 223 (80), 182 (42), 168 (32), 155 (47); ^1H NMR ($CDCl_3$) δ 7.66 (1 H, s, H-2), 7.50–6.94 (3 H, m, H-4, 6, 7), 6.10–5.53 (1 H, m, H-4′), 4.91–5.22 (2 H, m, H-5′), 4.30–4.10 (2 H, m, H-1′), 2.20–1.85 (4 H, m, H-2′,3′); peak matching calcd for $C_{14}H_{13}N_5$ 251.1172, found 251.1168. This azide was an unstable oil.

5-Azido-1-benzyl-3-cyanoindole (12d). 1-Benzyl-2-chloroindole-3-carboxaldehyde (**11d**)[27] (1.35 g, 5 mmol) was added to a mixture of NaN_3 (0.97 g, 15 mmol) in DMSO (15 mL) with stirring while the temperature was maintained at 88 °C. The temperature rose to 93 °C, and during 10 min 90 mL of N_2 was evolved (112 mL = 5 mmol). The reaction mixture was rapidly cooled and added to water (50 mL, 0 °C). The precipitated crystals were isolated, dried, and purified by column chromatography (SiO_2, ether/pentane (2:1)) to give light-sensitive crystals of **12d**: yield 0.45 g (33%), mp 111–112 °C (EtOH); IR (KBr) 2221, 2115 cm^{-1}; MS (m/z) 273 (M^+, 10), 245 (25), 91 (100), 65 (12); ^1H NMR ($CDCl_3$) δ 7.66 (1 H, s, H-2), 6.83–7.45 (8 H, m, aryl, H-6, H-7, H-4), 5.37 (2 H, s, CH_2). Anal. Calcd for $C_{16}H_{11}N_5$: C, 70.32; H, 4.06; N, 25.63. Found: C, 70.65; H, 4.08; N, 25.31. When the aqueous phase was acidified with HCl (4 M) extensive decomposition was observed.

3-Cyano-1-phenyl-2(3*H*)-indolone (13b). The aqueous phase from which compound **12b** was isolated was acidified with HCl (4 M) to pH = 5, and the precipitated crystals of **13b** were isolated and dried yielding 0.70 g (55%): mp 141–142 °C (EtOH); IR (KBr) 2228, 1736 cm^{-1}; MS (m/z) 234 (M^+, 100), 205 (95), 180 (10), 103 (26), 77 (40), 51 (52); ^1H NMR ($CDCl_3$) δ 7.60–6.83 (9 H, m, aryl, H-4, H-5, H-6, H-7), 3.73 (1 H, bs, exchange D_2O, H-3). Anal. Calcd for $C_{15}H_{10}N_2O$: C, 76.90; H, 4.30; N, 11.96. Found: C, 76.57; H, 4.30; N, 11.78.

Azide Rearrangement of 3-Acetyl-2-chloro-1-methylindole (16). A mixture of 3-acetyl-2-chloro-1-methylindole (**16**)[9] (1.04 g, 0.005 mol) and NaN_3 (0.97 g, 0.015 mol) in DMSO (15 mL) was heated at 120 °C for 3 min. Addition of the dark reaction mixture to water (50 mL) gave a semicrystalline product which was separated into two fractions using a Chromatotron (SiO_2, eluent ether/petroleum ether bp 80 °C): Fraction 1, 0.070 g of **18**; fraction 2, 0.111 g of **17**.

3-Cyano-1,2-dimethylindole (17): fraction 2, white crystals 111 mg (13.1%), mp 103–105 °C (lit.[11] mp 104–105 °C); IR (KBr) 2209 (CN) cm^{-1}; UV (abs EtOH) λ_{max} 287 (3.76), 280 (3.82), 222 (4.33); MS (m/z) 170 (M^+, 100), 155 (3), 140 (3), 128 (4), 115 (10); ^1H NMR ($CDCl_3$) δ 7.50–7.73 (1 H, m, H-5), 7.14–7.33 (3 H, m, H-4, H-6, H-7), 3.64 (3 H, s, NCH_3), 2.50 (3 H, s, CH_3).

3,8-Dimethylisoxazolo[3,4-*b*]indole (18): fraction 1, yellow crystals 70 mg (7.2%), mp 70–71 °C; IR (KBr) 1718 cm^{-1}; UV (abs EtOH) λ_{max} 402 (3.24), 259 (3.42), 234 (4.13); MS (m/z) 186 (M^+, 100), 171 (20), 157 (85), 143 (85), 102 (24); ^1H NMR ($CDCl_3$) δ 7.47–7.77 (2 H, m, H-6, H-5), 7.03–6.74 (2 H, m, H-4, H-7), 3.14 (3 H, s, NCH_3), 1.70 (3 H, s, CH_3). Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.77; H, 5.28; N, 14.70.

4-Cyano-5-methoxy-1-methyl-3-phenylpyrazole (19). To a solution of 4-cyano-5-hydroxy-1-methyl-3-phenylpyrazole (**3c**) (0.20 g, 0.001 mol) in acetone (25 mL) were added CH_3I (1 mL, 0.016 mol) and potassium *tert*-butoxide (0.118 g, 0.00105 mol). After stirring for 12 h at room temperature, saturated $NaHCO_3$ (30 mL) was added, and analytically pure **19** was isolated (1.20 g, 56%): mp 83–85 °C (cyclohexane); IR (KBr) 2216 cm^{-1}; MS (m/z) 213 (M^+, 100), 198 (22), 170 (52), 127 (22), 77 (9); UV (EtOH) λ_{max} 206 (4.26), 251 (3.89); ^1H NMR (DMSO-d_6) δ 8.00–7.47 (5 H, m, aryl), 4.33 (3 H, s, OCH_3), 3.69 (3 H, s, NCH_3); ^{13}C NMR (DMSO-d_6) δ 157.5 (C-5), 149.1 (C-3), 114.6 (CN), 71.4 (C-4), 60.4 (OCH_3), 34.1 (NCH_3), C_{aryl}: 131.3, 128.6, 125.1. Anal. Calcd for $C_{12}H_{11}N_3O$: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.56; H, 5.22; N, 19.73.

Mixture of Triazoles 20 and 21. A mixture of 1-(azidomethyl)-4-cyano-3-phenylpyrazole (**2c**) (2.24 g, 0.01 mol) and phenylacetylene (2.04 g, 0.02 mol) was refluxed in toluene (10 mL) for 14 h. Upon cooling, 2.93 g (91%) of yellow crystals separated. The product consisted (TLC) of **20** and **21** in the ratio 3:1 (^1H NMR) and was separated by fractional crystallization from toluene/petroleum ether.

1-[(4-Cyano-3-phenyl-1-pyrazolyl)methyl]-5-phenyltriazole (20). Separated from toluene/petroleum ether; after recrystallization the yield was 1.96 g (60%); mp 149–150 °C (toluene); IR (KBr) 2233 cm^{-1}; MS (m/z) 326 (M^+, 59), 298 (21), 182 (33), 158 (32), 130 (100), 129 (14), 103 (42); ^1H NMR (DMSO-d_6) δ 8.85 (1 H, s, H-5′), 7.98 (1 H, s, H-5), 7.82–7.49 (10 H, m, aryl), 6.84 (2 H, s, CH_2). Anal. Calcd for $C_{19}H_{14}N_6$: C, 69.93; H, 4.32; N, 25.75. Found: C, 69.95; H, 4.33; N, 25.72.

1-[(4-Cyano-3-phenyl-1-pyrazolyl)methyl]-4-phenyltriazole (21). Separated from toluene: yield 0.65 g (20%) mp 216–218 °C (toluene); IR (KBr) 2233 cm^{-1}; MS (m/z) relative intensity 326 (M^+, 17), 182 (27), 129 (100), 116 (34), 77 (26); ^1H NMR 9.08 (1 H, s, H-5), 8.86 (1 H, s, H-5′), 7.92–7.83 (4 H, m, aryl), 7.60–7.30 (6 H, m, aryl), 6.93 (2 H, s, CH_2). Anal. Calcd for $C_{19}H_{12}N_6$: C, 69.93; H, 4.32; N, 25.75. Found: C, 70.19; H, 4.35; N, 26.02.

5-Amino-3-cyano-1-methylindole (24). To a mixture of 5-azido-1-methylindole-3-carboxaldehyde (**12a**) (0.5 g, 0.025 mol) and $NaBH_4$ (0.07 g, 0.018 mol) in THF (8 mL) was added MeOH (0.4 mL) over 1 h at reflux temperature.[23] After cooling, HCl (1 M, 4 mL) was added and pH was adjusted to 10 with NaOH (10 M). Extraction with $CHCl_3$, drying (Na_2SO_4), concentration in vacuo, and recrystallization yielded **24**, 0.35 g (97%); mp 199–200 °C (EtOH); IR (KBr) 3382, 3120, 2212 cm^{-1}; MS (m/z) 171 (M^+, 100), 156 (25), 143 (4), 129 (5), 86 (10); ^1H NMR (DMSO-d_6) δ 7.97 (1 H, s, H-2), 7.24–7.43 (1 H, m, H-4), 6.63–6.82 (2 H, m, H-6, H-7), 5.00 (2 H, broad, exchange D_2O, NH_2), 3.80 (3 H, s, CH_3). Anal. Calcd for $C_{10}H_9N_3$: C, 70.16; H, 5.30; N, 24.54. Found: C, 70.29; N, 5.28; N, 24.52.