Synthesis of 5-Azido-4-cyanoimidazole and its Reaction with Active Methylene Compounds

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Diazotisation of 1-acetamido-5-amino-4-cyanoimidazole **2** using sodium nitrite in aqueous acetic acid gave 5-azido-4-cyanoimidazole **3** in 94% yield. Reaction of **3** with active methylene compounds $R^1COCH_2R^2$ [R^1 = Me, R^2 = COMe; R^1 = Me, R^2 = COPh; R^1 = Me, R^2 = COOEt] or malononitrile in the presence of base led either to imidazo[5,1-*d*][1,2,3,5]tetrazepines **6** and **8** or to imidazolyltriazoles **5**, **7** and **9**, depending on the reaction conditions. Tetrazepine **6c** evolves to triazole **7c** or **5c** respectively in the presence of acid or by further treatment with base. Purine **10** was also isolated in the reaction of **3** with malononitrile.

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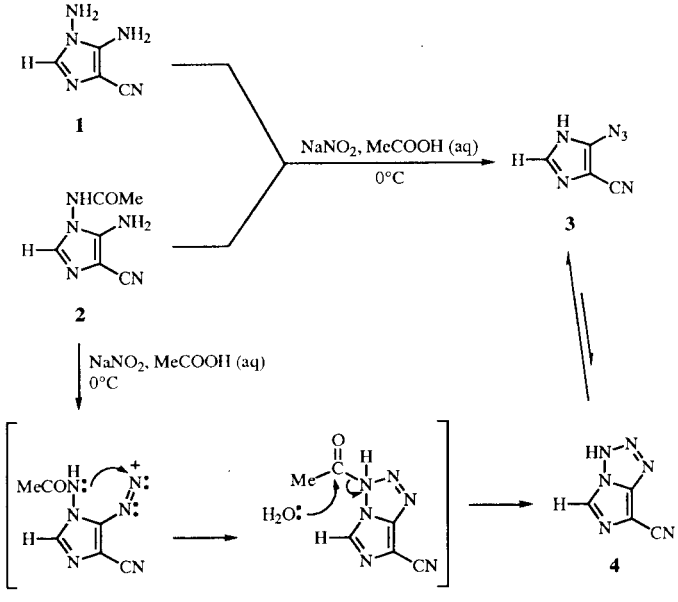
Alkyl, aryl and vinyl azides are well known compounds and their chemistry is well established [1]. In contrast, there have been few reports of compounds in which an azido group is bonded to a heterocyclic ring. Syntheses are known for 3-azidothiophenes [2], 5-azido-1,2,3-triazoles [3], and 2-azidoimidazoles [4]. There have been only three previous reports of the synthesis of 5-azidoimidazoles [5] and only a few reactions of this type of compound have been reported previously.

We now report a new and efficient method for the synthesis of 5-azido-4-cyanoimidazole **3** and its reaction with active methylene compounds in the presence of base (the Dimroth reaction). The Dimroth reaction leading to 1,2,3-triazoles is, of course, a well known reaction of alkyl, vinyl and aryl azides [6], and the 3-azidothiophens [2] and 5-azido-1,2,3-triazoles [3], have also been reported to undergo this reaction. To our knowledge there have been no previous reports of the similar reactions of 5-azidoimidazoles and we now describe our investigations of these reactions. It is clear from our observations that mechanistically these reactions of 5-azidoimidazole with active methylene compounds do not occur by the usual concerted 1,3-dipolar cycloaddition of the azide to the enolate, but 1,2,3-triazole formation proceeds by the initial formation of an imidazo[5,1-*d*][1,2,3,5]tetrazepine intermediate which can be isolated in some cases as the sodium salt.

Attempts to prepare 5-azido-4-cyanoimidazole **3** by diazotization of 1,5-diamino-4-cyanoimidazole **1** using sodium nitrite in aqueous acetic acid, at 0°, resulted in extensive decomposition of the reaction mixture and the desired product could only be isolated in 9% yield. It is known from other studies [7] that the amino group on N-1 is more reactive in substitution reactions than that in the 5 position. Hence, when N-1 is unprotected diazotization will occur at this more reactive position preferentially leading to loss of nitrogen and formation of decomposition products. Protection of the N-1 amine group should force reaction to occur at the desired 5-amino position. Thus, when 1-acetamido-5-amino-4-cyanoimidazole [8] **2** was used as the starting material, diazotization occured smoothly under similar reaction conditions to give **3** in 94% isolated yield. It is probable that the acetyl group participates in the reaction as shown in Scheme 1, and that the initial product of reaction is the imidazotetrazole **4**. Species **3** and **4** are likely to exist in equilibrium, as reported for

Scheme 1

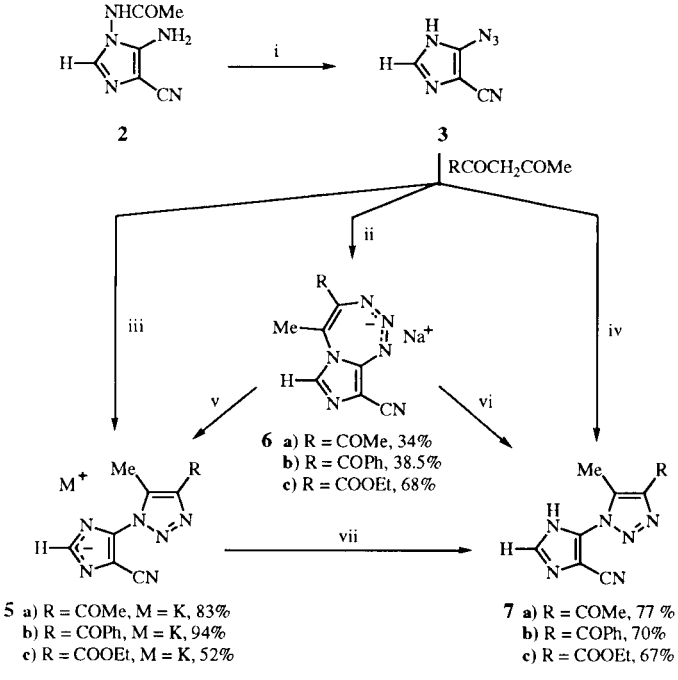


2-azidoimidazoles, where the equilibrium in the neutral species is mainly on the open-chain compound side [4]. In the present case, the open-chain structure **3** was assigned to the product mainly on the basis of ir data which showed two intense bands at 2122 and 2221 cm^{-1} assigned respectively to the stretching vibration of the cumulated double bond and of the C≡N.

Reproducing the experimental conditions described by Cottrell *et al.* [9] for the reaction of benzyl azides with active methylene compounds, a solution of **3** (1 equivalent) in ethanol was combined with the β-diketone (1.5 equivalent) and 1 equivalent of potassium carbonate in dimethyl sulfoxide (*ca.* 0.4 ml). The reaction was very slow (1-20 days) and structure **6** was assigned to the products isolated **6a-c**. The low yields (20-39%) derive from an inefficient ethyl acetate extraction. When compound **6c** was prepared following a similar experimental procedure but replacing ethanol by acetonitrile, the product precipitated out of solution and was isolated in 68% yield.

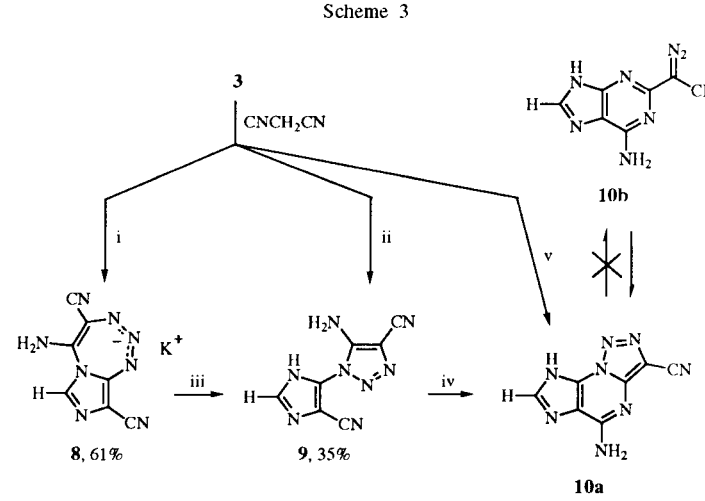
When a solution of **3** (1 molar equivalent) in tetrahydrofuran (THF) was added to a dilute solution of the active methylene compounds (1 molar equivalent) $MeCOCH_2R$ [R = COMe, COPh, COOEt] with sodium hydride (*ca.* 1.5 molar equivalents) in THF, under nitrogen, at room temperature, the reaction was faster (1-3 days) and the products **5** were isolated in the yields shown in Scheme 2. The same products were formed in similar yields by inverse addition of a solution of the sodium salt of the active methylene compound to a solution of azide **3** in THF. When a THF solution of **3** (1 molar equivalent) was treated with a mixture of the active methylene compound (1.1 molar equivalent) and sodium hydride (1-1.3 molar equivalents) in THF (*ca.* half the volume of solvent used in the previous reaction) under similar conditions, and the reaction mixture was then neutralized with concentrated hydrochloric acid, the products isolated were **7a-c**. There is no doubt that 1,2,3-triazoles formation occurs *via* the intermediate sodium salts **6a-c**. When a THF solution of **6c** was neutralized with concentrated hydrochloric acid, **7c** was obtained immediately in 58% yield. Further treatment of **6c** with a solution of sodium hydroxide in ethanol led to compound **5c** (as the sodium salt). Upon neutralization of **5c** with concentrated hydrochloric acid in THF, compound **7c** was isolated in 77% yield. Reaction between malononitrile and **3** to give **8** could, in our hands, only be carried out using potassium carbonate (1 equivalent) in dry dimethyl sulfoxide, at room temperature, and the product was isolated in 61% yield after dry flash chromatography. When this solution was neutralized with 1 equivalent of concentrated hydrochloric acid prior to the dry flash chromatography the purine **10a** was isolated in 61% yield. Neutralization of a THF solution of **8** gave the expected compound **9** in 34% yield. When 2 equivalents of potassium carbonate were used, compound **9** was isolated in 35% yield after neutralization and dry flash chromatography. The difficulty in this case is that there is competing formation of the

Scheme 2



i, $NaNO_2$, AcOH, H_2O; ii, K_2CO_3, DMSO, EtOH; iii, NaH, THF (9-12 ml); iv, 1. NaH, THF (2-4 ml) 2. HCl; v, NaOH, EtOH (**5c**, M = Na); vi, HCl, THF (**7c**, 58%); vii, HCl, THF (**7c**, 77%).

Scheme 3



i, K_2CO_3, DMSO, CH_3CN; ii, 1. K_2CO_3, DMSO 2. $HClO_4$; iii, HCl, THF (34%); iv, 1. NaH, THF 2. HCl (34%); v, 1. K_2CO_3, DMSO 2. HCl (61%).

Table 1

Physical and Analytical Data

Compound	Yield (%)	mp (°C)	Molecular Formula	Found: C, H, N (%)	Requires: C, H, N (%)	ms (70ev) m/z (%)
5a	83	>300 dec	$C_9H_7N_6ONa$	—	—	239 [(M+1)$^+$, 2] 192 (100)
5b	94	>300 dec	$C_{14}H_9N_6ONa$	55.8, 3.2, 27.7	56.0, 3.0, 28.0	—
5c	52	292-293 dec	$C_{10}H_9N_6O_2Na$	44.8, 3.3, 31.6	44.8, 3.4, 31.3	269 [(M+1)$^+$, 5] 247 (100)
9	35	>300 dec	$C_7H_4N_8$	hrms 201.0640	hrrns 201.0637	201 [(M+1)$^+$, 25] 137 (100)
7a	77	198-199 dec	$C_9H_8N_6O$	49.8, 3.9, 38.6	50.0, 3.7, 38.9	217 [(M+1)$^+$, 100]
7b	70	238-239 dec	$C_{14}H_{10}N_6O$	60.2, 3.6, 29.0	60.4, 3.6, 30.2	279 [(M+1)$^+$, 100]
7c	67	227-228 dec	$C_{10}H_{10}N_6O_2$	48.5, 4.1, 33.8	48.8, 4.1, 34.1	247 [(M+1)$^+$, 100]
8	61	>300 dec	$C_7H_3N_8K$	hrms 239.0196 hrms 201.0639	hrms 239.0196 hrms 201.0637	239 [(M+1)$^+$, 22], 201 [(M+1-K)$^+$, 63] 192 (100)
6a	34	284-285 dec	$C_9H_7N_6OK$	—	—	217 [(M+1-K)$^+$, 5] 176 (100)
6b	38.5	>300 dec	$C_{14}H_9N_6OK$	—	—	279 [(M+1-K)$^+$, 4.1] 176 (100)
6c	91	282-283 dec	$C_{10}H_9N_6O_2K$	—	—	247 [(M+1-K)$^+$, 75] 176 (100)
10a	61	>300	$C_7H_4N_8$	hrms 201.0628	hrms 201.0637	201 [(M+1)$^+$, 15] 154 (100)
3	94	>200 dec	$C_4H_2N_6$	35.5, 1.6, 63.0	35.8, 1.5, 62.7	135 [(M+1)$^+$, 5.3] 109 (100)

Table 2

^{1}H NMR and IR Data

Compound	IR (Nujol), ν (cm^{-1})	^{1}H NMR, δ, J (Hz)	Solvent
5a	2223 s, 1682 s, 1557 s, 1538 s	2.79 (3H, s, CH_3), 2.65 (3H, s, CH_3), 7.3 (1H, s, CH)	$(CD_3)_2SO$ [b]
5b [c]	2227 s, 1693 w, 1641 s, 1599 m, 1581 m, 1552 w, 1527 s	2.76 (3H, s, CH_3), 2.77 (3H, s, CH_3), 7.15 (1H, s, CH), 7.35 (1H, s, CH), 7.45 (5H, s, Ph), 7.7 (2H, t, J 8, *m*-ArH), 7.8 (1H, t, J 8, *p*-ArH), 8.3 (2H, d, J 8, *o*-ArH)	$(CD_3)_2SO$ [b]
5c	2231 s, 1744 s, 1703 s, 1578 w, 1538 s	1.45 (3H, t, J 7, CH_2CH_3), 2.65 (3H, s, CH_3), 4.45 (2H, q, J 7, CH_2CH_3), 7.32 (1H, s, CH)	$(CD_3)_2SO$ [b]
9	3386 m, 3300 m, 3213 m, 2237 m, 1640 s, 1600 s, 1574 m, 1503 w	7.8 (2H, br s, NH_2), 8.3 (1H, s, CH)	$(CD_3)_2SO$ [b]
7a	3114 s, 3075 m, 2226 m, 1657 s, 1595 m, 1535 s, 1508 m	2.7 (3H, s, $COCH_3$), 2.8 (3H, s, CH_3), 8.3 (1H, s, CH)	$(CD_3)_2SO$ [b]
7b	3119 s, 3057 m, 2225 m, 1652 s, 1595 s, 1585 m, 1577 m, 1535 s	2.85 (3H, s, CH_3), 7.65 (2H, t, J 8, *m*-ArH), 7.75 (1H, t, J 8, *p*-ArH), 8.25 (2H, d, J 8, *o*-ArH), 8.35 (1H, s, CH)	$(CD_3)_2SO$ [b]
7c	3302 s, 3125 s, 2244 m, 1737 s, 1595 s, 1553 m	1.45 (3H, t, J 7, CH_2CH_3), 2.8 (3H, s, CH_3), 4.45 (2H, q, J 7, CH_2CH_3), 8.35 (1H, s, CH)	$(CD_3)_2SO$ [b]
8	3435 m, 3310 m, 3190 m, 2245 m, 2213 s, 1642 s, 1579 s, 1556 w, 1538 m	7.7 (2H, br s, NH_2), 7.8 (1H, s, CH)	$(CD_3)_2SO$ [b]
6a	2215 s, 1670 s, 1560 m, 1530 s	—	—
6b	2215 s, 1690 m, 1645 s, 1595 m, 1575 m, 1550 m, 1525 s	—	—
6c	2214 s, 1697 s, 1569 m, 1537 m	1.4 (3H, t, CH_2CH_3), 2.7 (3H, s, CH_3), 4.5 (2H, q, J 7, CH_2CH_3), 7.8 (1H, s, CH)	$(CD_3)_2SO$ [b]
10a	3204 s, 3114 s, 2242 m, 1688 s, 1610 s, 1594 s, 1572 s, 1534 m, 1504 m	8.55 (1H, br s, CH), 8.6 (2H, br s, NH_2)	$(CD_3)_2SO$ [b]
3	3134 w, 3083 w, 2221 s, 2122 s, 1590 m, 1568 s, 1503 s	7.9 (1H, s, CH), 9.5-9.9 (1H, br s, NH)	$(CD_3)_2SO$ [a]

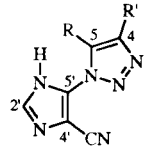
[a] Obtained using a 60 MHz machine. [b] Obtained using a 300 MHz machine. [c] The spectrum shows a set of bands assigned to the isomer where R = Ph, R^1 = COMe present in a ratio of 1:3.5.

purine **10**. This compound was isolated in 34% yield when **9** was treated with sodium hydride in THF followed by neutralization of the reaction mixture. In this reaction, the formation of a tricyclic purine derivative can occur by intramolecular nucleophilic attack of the amino substituent in the triazole ring, on the 5-cyano group in the imidazole. A similar situation has been previously reported in the reaction of 5-azido-4-cyano-1,2,3-triazole with active methylene compounds incorporating a cyano group [3]. The tricyclic triazolo-[1,5-*a*]pyrimidine isolated, equilibrates with the diazo form both in solution and in the solid state. In this case, the purine structure exists exclusively in the ring-closed form **10a**. There is no evidence for the presence of **10b** both in the ir and in the nmr spectra.

The structures of the new compounds were assigned on the basis of spectroscopic evidence and elemental analysis (see Tables). The existence of a tautomeric equilib-

Table 3

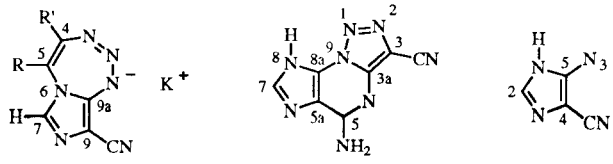
^{13}C NMR Chemical Shifts [δ_C $(CD_3)_2SO$] for 1-Imidazolyl-1,2,3-triazole and its Salts



Compound	R/R'	C-2'	C-4'	C-5'	C-4	C-5	CN	R	R'
5a	R = Me R' = COMe	149.0	106.9	144.0	141.4	146.6	122.2	13.8	31.7, 197.5
5b	R = Me R' = COPh	148.9	106.7	143.7	143.8	146.1	121.9	14.1	132.2, 134.0, 136.7, 190.7
	R = Ph R' = COMe	148.7	108.4	143.4	141.2	146.0	121.4	131.6 *o* 133.4 *m*	32.0, 196.0
5c	R = Me R' = CO2Et	148.8	106.7	143.8	139.2	142.8	121.9	13.6	18.1, 64.3, 165.1
9	R = Me R' = CN	142.8	97.2 br	144.6 br	105.0	151.8	115.1		117.0
7a	R = Me R' = COMe	142.9	99.4 br	144.9 br	142.3	147.0	114.8	13.8	31.8, 197.1
7b	R = Me R' = COPh	142.8	99.3 br	144.8 br	144.7	146.6	114.7	14.1	132.2 *m*, 134.0 *o*, 137.0 *p*, 140.8 *i*, 190.4
7c	R = Me R' = CO_2Et	143.0	99 v br	145 v br	140.9	144.0	114.9	13.9	18.3, 64.8, 164.8

Table 4

^{13}C NMR Chemical Shifts [δ_C $(CD_3)_2SO$] for Triazole **3**, Purine **10a** and Imidazo[5,1-*d*][1,2,3,5]tetrazepines

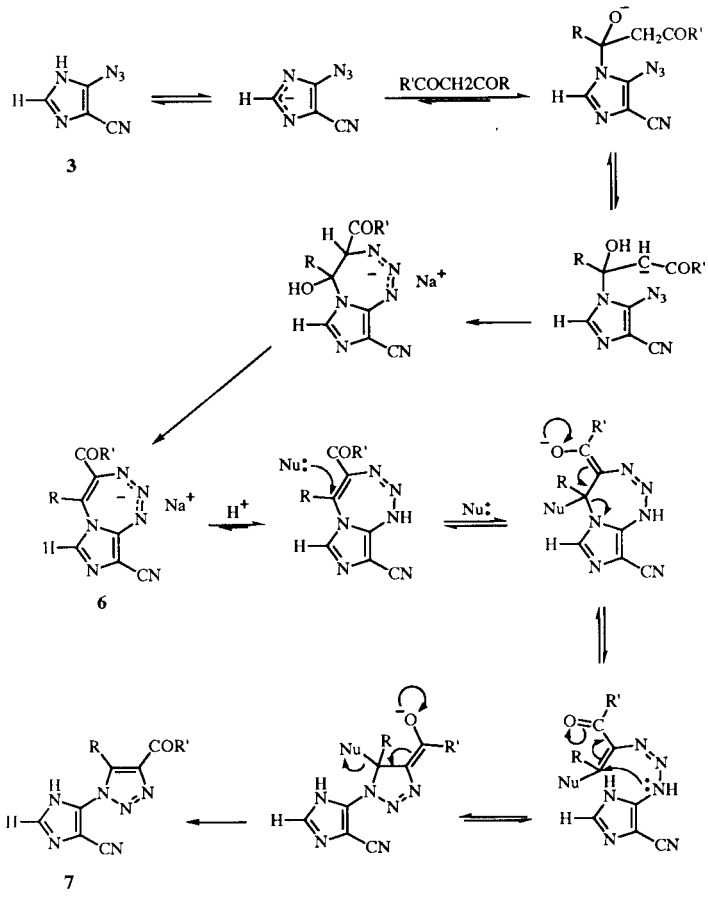


Compound	R/R'	C-2	C-3	C-3a	C-4	C-5	C-5a	C-7	C-8a	C-9	C-9a	CN	R	R'
8	$R = NH_2$ R' = CN	—	—	—	100.1	151.0	—	145.3	—	104.8	144.6	118.8	—	117.4
6c	R = Me $R' = CO_2Et$	—	—	—	139.8	143.7	—	146.0	—	103.3	144.4	118.5	13.8	18.2 64.6 165.0
10a	—	—	109.0	144.5	—	155.0	117.6	144.8	149.3	—	—	112.3	—	—
3	—	142.4	—	—	92.3	150.0	—	—	—	—	—	115.1	—	—

rium in the imidazole ring of compounds **7a-c** and **9** was noted in the ^{13}C nmr spectra which showed broad bands in the δ 97-99 and δ 144-145 ppm region assigned respectively to C-4' and C-5'. The C-2' carbon always appears as a signal around δ 143 ppm and the nitrile carbon atom was at *ca.* δ 115 ppm. In contrast, in the ^{13}C nmr spectra of compounds **5a-c**, the bands assigned to the imidazole carbon atoms C-2', C-4' and C-5' are sharp and appear around δ 149, 107 and 144 ppm respectively. For compounds **6a-c** and **8** sharp bands were also observed for C-7, C-9 and C-9a, respectively in the region of δ 146, 104 and 145 ppm. The absence of the N-H bond in these compounds is confirmed by the absence of absorptions in the 3000-4000 cm^{-1} region of the ir spectra.

It is usually regarded that reactions between azides and active methylene compounds occur either by attack by the carbanion on the terminal nitrogen atom of the azide to give a triazene intermediate, followed by cyclization and aromatization to the triazole, or by a concerted 1,3-dipolar cycloaddition of the azide to the enolate [1a]. In our reactions this is clearly not the case as the initial product in all cases is the salt of the imidazo[5,1-*d*][1,2,3,5]tetrazepine **6a-c** and **8**. We believe that this intermediate is formed by initial formation of the imidazole anion which attacks the carbonyl com-

Scheme 4



pound according to the mechanism shown in Scheme 4. The rearrangement of **3** to **4** could be explained by an acid or base catalyzed ring opening of the seven-membered ring followed by ring closure to the more stable 1,2,3-triazole.

EXPERIMENTAL

The ^1H nmr spectra were recorded on Hitachi-Perkin-Elmer R24B (60 MHz) or Bruker XL300 (300 MHz) instruments (with J-values given in Hz), ^{13}C nmr spectra (with DEPT 135) either on a Bruker WP80 or XL300 instrument, and ir spectra on a Shimadzu IR-435. Mass spectra were recorded on a Kratos Concept instrument and uv spectra on a Perkin-Elmer Lamda 15 uv/vis spectrometer. The melting points were measured on an Electrothermal digital melting point apparatus and are uncorrected. Physical and spectroscopic data for compounds **3-10** are given in Tables 1-4. Sodium hydride was kept under nitrogen atmosphere and was washed twice with petroleum ether (40-60) through a serum cap, before each reaction.

Preparation of 5-Azido-4-cyano-1*H*-imidazole (**3**).

An aqueous solution of sodium nitrite (0.19 g, 2.79 mmoles) in distilled water (2 ml) was added to a solution of 1-acetamido-5 amino-4-cyanoimidazole [1] **2** (0.43 g, 2.58 mmoles) in distilled water (5 ml) with stirring in an ice bath. On addition of glacial acetic acid (0.29 ml, 5.16 mmoles) the solution turned pink and a solid started to precipitate. Another molar equivalent of sodium nitrite (0.19 g, 2.79 mmoles in water 3 ml) was added. The solid was filtered off, washed with water and dried under vacuum to give a light orange solid (0.21 g). The filtrate was extracted with diethyl ether (6 x 15 ml) and the extracts were combined and dried with magnesium sulphate. The solvent was partly removed in the rotary evaporator, petroleum ether (40-60) was added and the solid was filtered off and washed with petroleum ether to give 5-azido-4-cyano-1*H*-imidazole (**3**) (0.33 g, 94%), mp >200° dec.

General Procedure for the Preparation of the Potassium Salt of Imidazolyltriazoles **5a-c**.

A solution of azide **3** (1 molar equivalent) in THF (5 ml) was added to a suspension of sodium hydride (1.5-1.7 molar equivalents) in dry THF (5 ml). The ketone (1-1.2 molar equivalents) was added and the mixture was stirred at room temperature until tlc showed that all the starting material had been consumed (usually 18 hours-3 days). The solid was isolated by filtration and washed with diethyl ether to give the analytically pure product in the yields shown in Table 1.

General Procedure for the Preparation of Imidazolyltriazoles **7a-c**.

The diketone (1-1.2 molar equivalents) was added to a suspension of sodium hydride (1-1.5 molar equivalents) in dry THF (2-4 ml). A solution of azide **3** (1 molar equivalent) in THF (2 ml) was added slowly with a syringe, to the previous mixture, which was stirred at room temperature until tlc showed that all the starting material had been consumed (usually 2-8 days). Neutralization with concentrated hydrochloric acid (1 molar equivalent) led to the precipitation of sodium chloride which was filtered and washed with THF. Concentrating the solution led to a pinkish solid which was filtered and washed with chloroform and diethyl ether. The solid was dried under vacuum to give analytically pure product in the yields shown in Table 1.

General Procedure for the Preparation of Imidazo[5,1-*d*]-[1,2,3,5]tetrazepines **6a-c**.

Potassium carbonate (1 molar equivalent) and the β-diketone (1.5 molar equivalents) were added to a solution of azide **3** (1 molar equivalent) in absolute ethanol (5-10 ml). Dimethyl sulfoxide (0.3 ml) was added and the mixture was stirred at room temperature until tlc showed that all the starting material had disappeared (usually 1-20 days). Water (5-7 ml) was added and the mixture was extracted with diethyl ether (to remove the excess of diketone) and then with ethyl acetate. The extracts were combined and dried with potassium carbonate, and the product precipitated as a yellow solid after partial evaporation of the solvent and addition of chloroform. The solid was washed with chloroform and diethyl ether and was dried under vacuum to give the analytically pure product in the yields shown in Table 1.

Reaction of 5-Azido-4-cyano-1*H*-imidazole (**3**) with Malononitrile.

Method A.

Potassium carbonate (0.45 g, 3.25 mmoles) was added to a solution of malononitrile (0.21 g, 3.25 mmoles) in dimethyl sulfoxide (0.6 ml). A solution of azide **3** (0.22 g, 1.6 mmoles) in dimethyl sulfoxide (0.4 ml) and acetonitrile (10 ml) was added dropwise over a period of 8 hours, while the mixture was stirred at room temperature. Tlc showed that all the starting material had

been consumed and a yellow solid was isolated after dry flash chromatography on the reaction mixture (ethyl acetate eluant). The solid was filtered and washed with ethyl acetate and diethyl ether and identified as the potassium salt of 7-amino-4-cyano-imidazo[5,1-*d*][1,2,3,5]tetrazepine (**8**) (0.23 g, 1.0 mmole, 61%).

Method B.

Malononitrile (0.07 g, 1.1 mmoles) was added to a suspension of potassium carbonate (0.39 g, 2.8 mmoles) in dimethyl sulfoxide (2 ml). The mixture was stirred at 20° while a solution of azide **3** (0.10 g, 0.7 mmole) in dimethyl sulfoxide (0.5 ml) was added dropwise over a period of 8 hours. As tlc showed that all the starting material had been consumed, the excess of potassium carbonate was filtered and perchloric acid was added to the solution until carbon dioxide evolution ceased. A pinkish solid was isolated after dry flash chromatography (chloroform eluant), which was filtered and washed with chloroform. The solid was identified as imidazolyltriazole **9** (0.05 g, 0.25 mmole, 35%).

Method C.

Malononitrile (0.08 g, 1.2 mmoles) was added to a suspension of potassium carbonate (0.15 g, 1.1 mmoles) in dimethyl sulfoxide (1 ml). The mixture was stirred at 5-10° while a solution of azide (**3**) (0.11 g, 0.82 mmole) in dimethyl sulfoxide (0.5 ml) was added dropwise. As tlc showed that all the starting material had been consumed, the solution was neutralized with concentrated hydrochloric acid (0.09 g, 1.1 mmoles). A pinkish solid was isolated after dry flash chromatography (acetone eluant), which was filtered and washed with ethanol and diethyl ether. The solid was identified as purine **10a** (0.10 g, 0.50 mmole, 61%).

Rearrangement of Imidazo[5,1-*d*][1,2,3,5]tetrazepine (**6c**).

Concentrated hydrochloric acid (0.005 ml, 0.06 mmole) was added to a suspension of **6c** (0.015 g, 0.06 mmole) in THF (3 ml). A homogeneous solution was obtained, and shortly after a white solid (sodium chloride) precipitated out of solution and was filtered through fibre-glass paper. The solution was evaporated in the rotary evaporator leading to a yellow solid identified as **7c** (0.009 g, 0.04 mmole, 58%).

Rearrangement of Imidazo[5,1-*d*][1,2,3,5]tetrazepine (**8**).

Method A.

Concentrated hydrochloric acid (0.008 ml, 0.10 mmole) was added to a suspension of **8** (0.02 g, 0.09 mmole) in THF (5 ml). The solid product precipitated from solution together with potassium chloride and the mixture was concentrated in the rotary evaporator. A pinkish solid was isolated by filtration (0.013 g). Compound **9** was the only organic material present in the solid mixture, according to spectroscopic evidence.

Method B.

A suspension of **9** (0.06 g, 0.24 mmole) in THF (8 ml) was added to a suspension of sodium hydride (0.008 g, 0.32 mmole) in THF (2 ml) and the mixture was stirred at room temperature for 2 hours. The solid suspension was filtered and neutralized with concentrated hydrochloric acid (0.024 ml, 0.29 mmole). Concentration of the reaction mixture in the rotary evaporator led to a white solid (0.06 g). Compound **10** was the only organic material present in the solid mixture, according to spectroscopic evidence.

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