"One Pot" Synthesis of 2,9-Disubstituted 8-Azaadenines
(3,5-Disubstituted 7-Amino-3H-1,2,3-triazolo[4,5-d]pyrimidines)

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A new simple method for the synthesis of title compounds is described starting from malononitrile, benzyl-azide and an aliphatic or aromatic nitrile.

Recently, we have obtained a quick and nearly general synthetic method for 3-benzyl-5-substituted-7-hydroxy-3H-1,2,3-triazolo[4,5-d]pyrimidines **I** (Scheme 1) [1], which after debenzylation should probably show inhibitory activity against xanthine oxidase. According to this approach we prepared also some 2-aminomethyl-8-azahypoxanthine (2-homo-8-azaguanine) derivatives [2].

Scheme 1
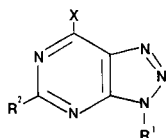
I) X = OH ; R¹ = CH₂C₆H₅ ; R² = alkyl or aryl group [1]
II) X = NH₂ ; R¹ = CH₂C₆H₅ ; R² = alkyl or aryl group (Table 1)

Successively we become interested in the synthesis of 6-amino-8-azapurines (8-azaadenines) bearing a substituent on C-2 (**II**, Scheme 1), due to their absence in the literature.

Since the *in vitro* metabolic pathways followed by 8-azaadenosine, 8-azainosine and 8-azaguanine were uncovered [3-9], compounds **II** might be interesting as antimetabolites (Scheme 1, R¹ = H); in fact, on the basis of this hypothesis, compounds **II** could be activated to azanucleotides and successively incorporated into RNA. Further, adenine nucleoside analogs of chemotherapeutic interest as antitumor or antiviral agents are hydrolytically deaminated by adenosine deaminase (ADA) to inactive or considerably less active hypoxanthine analogs [10]. It was demonstrated that, among ADA inhibitors, formycin [11], coformycin [12], and 2'-deoxycoformycin (pentostatin) [13,14] are able to enhance the cytotoxic activity of many adenosine analogs such as 8-azaadenosine. The secondary unwilling effect of pentostatin prompted Montgomery and coworkers to synthesize some adenosine and 8-azaadenosine derivatives [15]. Among these compounds, 2-fluoro-8-azaadenosine is deaminated more slowly with respect to adenosine

and exhibited some cytotoxic effect. These findings indicated that structural analogs of adenine or adenosine, which are relatively poor substrates of ADA, could show interesting antineoplastic properties.

In the aim of obtaining some further information about the structural requisites of a molecule which is able to inhibit the enzymes of purine catabolism we were engaged not long ago in the need to obtain 2-substituted and 2,9-disubstituted 8-azapurines. Indeed, in our mind, the introduction of a substituent on C-2 could give some information on this topic.

The classical route to 2-unsubstituted 8-azaadenines starts from 4,5-diamino-6-chloropyrimidines which can be treated with nitrous acid and ammonia, successively [16]. Another method employs the 6-hydroxy derivatives (8-azahypoxanthines) *via* the 6-chloro compounds [17]. 2-Unsubstituted or substituted 8-azahypoxanthines have also been synthesized by cycling appropriately substituted 1,2,3-triazoles with formamide [18], urea [19], or amidines (few examples) [20]. More recently, 2-aryl-8-azahypoxanthines were prepared from aryl amidines [21,22].

A synthetic approach to the title compounds might be attempted on the basis of the well known heteroanulation of aromatic *o*-aminonitriles in the presence of a nitrile and hydrogen chloride [23,24]. This reaction produces a 6-aminopyrimidine fused on the 4,5-position with the aromatic nucleus of the *o*-aminonitrile (Scheme 2, path **a**). On the other hand, we could have attempted a base catalysed ring closure of the appropriate compounds [25,26] (Scheme 2, path **b**). In both these methods we must start from 1-substituted 4-cyano-5-aminotriazoles or their 5-acylamino derivatives, respectively. In this regard, we have verified that the base catalysed reaction of 1-unsubstituted 4-cyano-5-tosylamino-1,2,3-triazole [27] with nitriles was unsuccessful.

According to literature reports, 1-benzyl-4-cyano-5-amino-1H-1,2,3-triazole (**III**) can be obtained from the corresponding 4-carbamoyl compound with phosphorus oxy-

Scheme 2

Scheme 3

Scheme 4
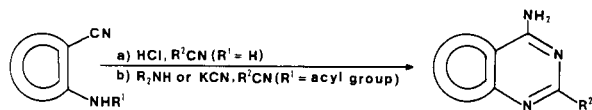
chloride in DMF [28] or from malononitrile and benzyl-azide by a sodium ethoxide catalysed 1,3-dipolar cycloaddition [29]. This latter method seemed to be the best way for a "one pot" procedure. The above authors described a low yield preparation of this compound by conducting the reaction at room temperature; they also isolated 1-benzyl-4-carboiminoethoxy-5-amino-1H-1,2,3-triazole and a high melting product to which the structure IV (Scheme 3) was assigned [28]. A similar compound was obtained with phenylazide [30]. Compound IV, because of its "dimeric" structure, certainly originated from two molecules of the 4-cyano-5-amino-1H-1,2,3-triazole through an intermolecular nucleophilic attack of an amino group with a cyano group. A similar dimerisation for o-aminobenzonitriles was first observed by Taylor et al. [31,32].
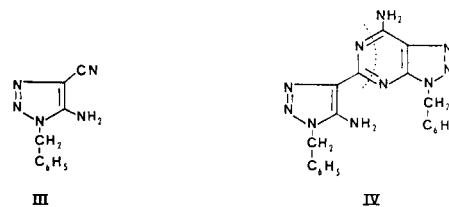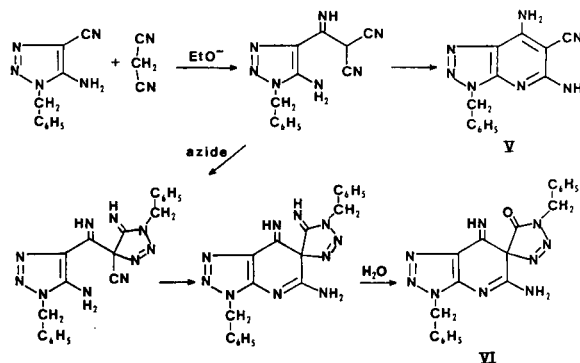
Table 1

Starting nitrile [X]	Reaction product II	Reaction time (hours)	Yields (%)	Mp°C [Y]	Molecular formula	Analyses % Calcd./Found			Dimer IV yields (%)
						C	H	N	
CH_3CN [15]	1, $R^2 = CH_3$	4	36	255-257 [a]	$C_{12}H_{12}N_6$	59.98 59.75	5.03 5.10	34.98 34.96	12
CH_3CH_2CN [15]	2, $R^2 = CH_2CH_3$	4	31	206-208 [b]	$C_{13}H_{14}N_6$	61.40 61.42	5.55 5.58	33.05 33.05	7.5
C_6H_5CN [10]	3, $R^2 = C_6H_5$	4	32	195-197 [a]	$C_{17}H_{14}N_6$	67.53 67.43	4.67 4.66	27.80 27.61	10
$o\text{-}CH_3C_6H_4CN$ [10]	4, $R^2 = o\text{-}CH_3C_6H_4$	4	13	185-187 [b]	$C_{18}H_{16}N_6$	68.33 68.35	5.10 5.20	26.57 26.37	13
$m\text{-}CH_3C_6H_4CN$ [10]	5, $R^2 = m\text{-}CH_3C_6H_4$	4	35	192-194 [a]	$C_{18}H_{16}N_6$	68.33 68.25	5.10 5.15	26.57 26.40	7.5
$p\text{-}CH_3C_6H_4CN$ [10]	6, $R^2 = p\text{-}CH_3C_6H_4$	4	44	199-201 [b]	$C_{18}H_{16}N_6$	68.33 68.27	5.10 5.25	26.57 26.45	12
$o\text{-}ClC_6H_4CN$ [3]	7, $R^2 = o\text{-}ClC_6H_4$	4	34	234-236 [c]	$C_{17}H_{13}ClN_6$	60.62 60.55	3.89 3.95	24.96 24.85	10
$m\text{-}ClC_6H_4CN$ [3]	8, $R^2 = m\text{-}ClC_6H_4$	4	45	243-245 [c] + [a]	$C_{17}H_{13}ClN_6$	60.62 60.50	3.89 3.85	24.96 24.90	5.5
$p\text{-}ClC_6H_4CN$ [3]	9, $R^2 = p\text{-}ClC_6H_4$	4	31	223-225 [b]	$C_{17}H_{13}ClN_6$	60.62 60.42	3.89 3.90	24.96 24.96	—
$2\text{-}C_5H_4NCN$ [1]	10, $R^2 = 2\text{-}C_5H_4N$	1.5	38	221-223 [b]	$C_{16}H_{13}N_7$	63.35 63.75	4.32 4.40	32.33 32.25	4
$3\text{-}C_5H_4NCN$ [1]	11, $R^2 = 3\text{-}C_5H_4N$	1.5	62	270-272 [b]	$C_{16}H_{13}N_7$	63.35 63.45	4.32 4.45	32.33 32.20	12
$4\text{-}C_5H_4NCN$ [1]	12, $R^2 = 4\text{-}C_5H_4N$	1.5	65	253-255 [a]	$C_{16}H_{13}N_7$	63.35 63.40	4.32 4.30	32.33 32.20	—

[X] = Molar ratio: nitrile/azide.   [Y] = Crystallisation solvent: [a] = methanol, [b] = ethanol, [c] = chloroform.

Table 2

IR ν (cm^{-1}) and PMR δ (ppm) Data

1   ir: 3125, 3325 (NH$_2$); pmr: 2.45 (s, CH$_3$, 3H), 5.71 (s, CH$_2$, 2H), 7.31 (s, aromatic, 5H), 8.11 (br s, NH$_2$, 2 exchangeable H)

2   ir: 3125, 3330 (NH$_2$); pmr: 1.26 (t, CH$_3$, 3H, J = 7.3 Hz), 2.72 (q, CH$_2$, 2H, J = 7.3 Hz), 5.71 (s, CH$_2$, 2H), 7.33 (s, aromatic, 5H), 8.08 (br s, NH$_2$, 2 exchangeable H)

3   ir: 3140, 3270, 3445 (NH$_2$); pmr: 5.81 (s, CH$_2$, 2H), 7.38 (m, aromatic, 5H), 7.49 (m, aromatic, 3H), 8.23 (br s, NH$_2$, 2 exchangeable H), 8.44 (m, aromatic, 2H)

4   ir: 3140, 3300, 3360 (NH$_2$); pmr: 2.47 (s, CH$_3$, 3H), 5.78 (s, CH$_2$, 2H), 7.31 (m, aromatic, 3H), 7.35 (s, aromatic, 5H), 7.75 (m, aromatic, 1H), 8.26 (br s, NH$_2$, 2 exchangeable H)

5   ir: 3150, 3280, 3440 (NH$_2$); pmr: 2.41 (s, CH$_3$, 3H), 5.82 (s, CH$_2$, 2H), 7.34 (m, aromatic, 3H), 7.37 (s, aromatic, 5H), 8.26 (m, aromatic, 1H), 8.26 (br s, NH$_2$, 2 exchangeable H)

6   ir: 3165, 3290, 3495 (NH$_2$); pmr: 2.37 (s, CH$_3$, 3H), 5.80 (s, CH$_2$, 2H), 7.30 (d, aromatic, 2H, J = 8.1 Hz), 7.36 (s, aromatic, 5H), 8.30 (br s, NH$_2$, 2 exchangeable H), 8.33 (d, aromatic, 2H, J = 8.1 Hz)

7   ir: 3145, 3315, 3370 (NH$_2$); pmr: 5.78 (s, CH$_2$, 2H), 7.36 (m, aromatic, 5H), 7.51 (m, aromatic, 3H), 8.31 (br s, NH$_2$, 2 exchangeable H), 8.35 (m, aromatic, 1H)

8   ir: 3155, 3300, 3460 (NH$_2$); pmr: 5.84 (s, CH$_2$, 2H), 7.37 (m, aromatic, 5H), 7.48 (m, aromatic, 2H), 8.38 (m, aromatic, 2H), 8.40 (br s, NH$_2$, 2 exchangeable H)

9   ir: 3150, 3285, 3450 (NH$_2$); pmr: 5.81 (s, CH$_2$, 2H), 7.36 (m, aromatic, 5H), 7.54 (d, aromatic, 2H, J = 8.7 Hz), 8.30 (br s, NH$_2$, 2 exchangeable H), 8.42 (d, aromatic, 2H, J = 8.7 Hz)

10   ir: 3100, 3475 (NH$_2$); pmr: 5.86 (s, CH$_2$, 2H), 7.36 (s, aromatic, 5H), 7.51 (m, aromatic, 1H), 7.95 (m, aromatic, 1H), 8.40 (m, aromatic, 1H), 8.45 (br s, NH$_2$, 2 exchangeable H), 8.74 (m, aromatic, 1H)

11   ir: 3260, 3345 (NH$_2$); pmr: 5.84 (s, CH$_2$, 2H), 7.39 (m, aromatic, 5H), 7.46 (m, aromatic, 1H), 8.35 (br s, NH$_2$, 2 exchangeable H), 8.68 (m, aromatic, 2H), 9.55 (m, aromatic, 1H)

12   ir: 3280, 3350 (NH$_2$); pmr: 5.84 (s, CH$_2$, 2H), 7.38 (m, aromatic, 5H), 8.27 (m, aromatic, 2H), 8.33 (br s, NH$_2$, 2 exchangeable H), 8.74 (m, aromatic, 2H)

Therefore we have studied this reaction in more detail. During preliminary experiments conducted in refluxing ethanol, we obtained the dimer **IV** as the prevalent product. Small amounts of **III** as well as of two other by-products, **V** and **VI**, were isolated by preparative tlc. On the basis of elemental analysis and spectroscopic characteristics of these two compounds, we were able to assign their chemical structures and to outline route for their formation (Scheme 4).

Notwithstanding these facts, and keeping in mind the formation of dimer **IV**, *i.e.* the aptitude of the amino group of the triazole **III** to react with a cyano group, we tried to form **II** to compete with the dimerisation by adding a nitrile to the reaction mixture. In this way the preparation of title compounds **II** was successful (Scheme 5, path **b**). *A priori*, this approach could be considered prac-

ticable in case that the rate of process *a* was low on respect of *b* and *c*, which presumably are second order reactions. Moreover, supposing that the numerical values of kinetic constants, K_b and K_c, were not very different, we added a mixture of azide and nitrile in appropriate molar ratio to the sodium salt of malononitrile. In this manner the formation of **II** was prevalent. The quantitative ratio of the nitrile with respect to azide and the reaction time were established in connection with the relative reactivity of the nitrile itself (Table 1). The excess nitrile could be recovered after neutralisation and fractional distillation under reduced pressure of the reaction mixture. The dimer **IV** was in part separated in many cases by diluting the residue with chloroform in which it is slightly soluble. Compounds **V** and **VI** were always present as negligible by-products in the reaction mixtures of less reactive nitriles.

Scheme 5
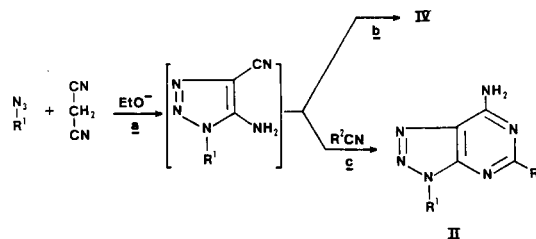
The yields of this "one pot" preparation of 2-substituted 8-azaadenines **II** are moderately good, considering that their isolation was based on repeated fractional crystallizations after the above work up. In the case of pyridinenitriles the best yields were obtained. Tetrazoles were never isolated probably because of the mild reaction conditions [33]. Adducts **II** were characterised by analytical and spectroscopic data (Table 1, 2, 3).

In our opinion the products **II** (R^1 = H) which could be eventually obtained by debenzylation may be interesting as inhibitors of ADA and as cytotoxic agents.

At the moment, we are studying procedures to obtain structurally more complex azides in order to generalize the present synthetic method and to obtain compounds **II** that may be interesting from a medicinal point of view.

EXPERIMENTAL

Table 3

CMR Data (ppm) [34]

II	C-3a	C-5	C-7	C-7a	CH$_2$	Benzylic Carbons				R^2 Carbons							
						C'-1 [a]	C'-2	C'-3	C'-4	C"-1 [a]	C"-2	C"-3	C"-4	C"-5	C"-6	CH$_2$	CH$_3$
1	155.8	166.4	149.8	122.5	19.1	136.0	127.9	127.6	128.7	—	—	—	—	—	—	—	25.7
2	156.0	170.5	149.8	122.7	49.1	135.9	127.9	127.8	128.7	—	—	—	—	—	—	32.0	12.6
3	156.1	162.1	150.1	123.1	49.4	135.9	128.3	128.0	128.7	135.7	128.3	128.0	130.5	—	—	—	—
4	155.9	165.2	149.6	122.4	49.5	135.9	128.7	127.9	127.9	138.5	136.7	130.8	128.9	125.3	130.1	—	21.0
5	156.1	162.3	150.1	123.1	49.4	135.9	128.7	127.3	127.3	137.5	137.3	131.2	125.6	128.1	128.9	—	21.1
6	156.0	162.3	150.1	123.0	49.3	135.9	128.7	127.9	127.9	140.3	128.9	128.3	134.9	—	—	—	20.9
7	156.1	163.3	149.4	122.7	49.5	135.8	128.7	128.0	128.0	138.5	131.4	130.2	131.2	126.8	129.8	—	—
8	156.1	160.6	150.0	123.2	49.5	135.8	128.7	128.0	128.0	139.6	130.3	133.3	126.7	128.4	130.3	—	—
9	156.1	161.0	150.0	123.1	49.4	135.9	128.7	128.0	128.0	136.4	130.0	128.4	135.5	—	—	—	—
10	156.4	162.0	150.1	123.2	49.4	135.9	129.7	127.8	127.9	155.0	—	123.8	124.8	149.3	136.7	—	—
11	156.1	160.4	149.8	123.2	49.5	135.8	128.0	128.0	128.7	155.1	123.5	—	132.9	135.4	149.4	—	—
12	156.3	160.1	149.9	123.5	49.6	135.7	128.7	128.0	128.0	144.7	150.2	122.1	—	—	—	—	—

[a] = Quaternary carbons.

General Procedure for the Preparation of Compounds **II**.

To a stirred hot ethanolic solution of sodium ethoxide obtained from sodium (0.27 g, 0.012 g-atom) and anhydrous ethanol (20 ml), malononitrile (0.66 g, 0.01 mole) was added. Into the formed salt solution a mixture of benzylazide (1.33 g, 0.01 mole) and a nitrile (0.01-0.15 mole) was dropped. Heating was continued for the time indicated in Table 1. Dilution with ethanol, mild acidification with acetic acid of Dowex-H$^+$ resin, filtration and evaporation of the solvent left a residue from which an excess of high boiling nitrile was fractionated under reduced pressure. The solid residue was then treated with chloroform (200 ml) and the suspension was stirred for 30 minutes. Dimer **IV** was filtered off and the solution was evaporated under reduced pressure. Some compounds **II**, as the pyridyl derivative, are almost insoluble in chloroform, but in these cases dimer **IV** was formed in a negligible amount. In other cases separation of **II** from **IV** required very tedious fractional crystallization (Table 1).

3-Benzyl-5,7-diamino-6-cyano-3H-1,2,3-triazolo[4,5-b]pyridine (**V**) and Spiro[6,7-dihydro-3-benzyl-5-amino-7-imino-3H-1,2,3-triazolo[4,5-b]pyridine-6,4'-(4',5'-dihydro-1'-benzyl-5'-oxo)-1'H-1',2',3'-triazole] (**VI**).

They were isolated by preparative tlc of a chloroform solution of the solid residue obtained after work up from malononitrile and benzyl azide under the above reaction conditions: Compound **V** had Rf 0.6 (ethyl acetate/acetone 9:1), mp 304-306° (ethanol); ir: 3160, 3320, 3380, 3420 (NH$_2$), 2190 (CN); pmr: 5.55 (s, CH$_2$, 2H), 6.71 (br s, NH$_2$, 2 exchangeable H), 7.29 (s, aromatic, 5H), 7.83 (br s, NH$_2$, 2 exchangeable H).

Anal. Calcd. for C$_{13}$H$_{11}$N$_7$: C, 58.87; H, 4.15; N, 36.98. Found: C, 58.65; H, 4.05; N, 36.85.

Compound **VI** had Rf 0.4 (ethyl acetate/acetone 9:1), mp 300-303° dec (ethanol); ir: 3300, 3350, 3400 (NH$_2$ + NH), 1715 (CO); pmr: 5.54 (s, CH$_2$, 2H), 5.88 (s, CH$_2$, 2H), 6.96 (br s, NH$_2$, 2 exchangeable H), 7.34 (s, aromatic, 10 H), 12.12 (br s, NH, 1 exchangeable H).

Anal. Calcd. for C$_{20}$H$_{17}$N$_9$O: C, 60.15; H, 4.26; N, 31.57. Found: C, 60.05; H, 4.10; N, 31.65.

Compound **IV** had Rf 0.15 (ethyl acetate/acetone 9:1), mp 255-257° (pyridine/water) [28]; ir: 3140, 3180, 3310, 3420 (NH$_2$); pmr: 5.49 (s, CH$_2$, 2H), 5.79 (s, CH$_2$, 2H), 6.89 (br s, NH$_2$, 2 exchangeable H), 7.31 (s, aromatic, 10 H), 8.27 (br s, NH$_2$ 2 exchangeable H).

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[34] Since the literature ^{13}C nmr data regarding analogous compunds [1] have been scarcely reported, we have tentatively assigned the chemical shifts.