1,2,3-Triazoles. Part I. Some 4-Aminotriazole-5-carbaldehydes †

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4-Amino-1-(2- and 3-)methyl-1,2,3-triazole-5-carbaldehydes (1a—c) were made from the corresponding 5-carbonitriles by catalytic hydrogenation over palladium in hydrochloric acid of a critical strength. The 3-benzyl analogue was prepared by the same method. This and the 2-methyl analogue were also made by esterification of 4-amino-2-methyl-(or 3-benzyl-)1,2,3-triazole-5-carboxylic acid, followed by reduction of the product to give the 5-hydroxymethyl derivative [*e.g.* (3)] which was oxidized with manganese dioxide to the aldehyde. When 4-amino-2-methyl-1,2,3-triazole-5-carbonitrile was hydrogenated in the presence of phenylhydrazine, phenylsemicarbazide, or hydrazine hydrate, the phenylhydrazone, phenylsemicarbazone, or azine of the aldehyde were formed, but the free aldehyde could not be liberated from these derivatives. 4-Amino-1-methyl-1,2,3-triazole (5) was made by decarboxylating the 5-carboxylic acid. Dehydration of 4-amino-1,2,3-triazole-5-carboxamide with thionyl chloride in pyridine gave 4-amino-1-(2- or 3-)(4-pyridyl)-1,2,3-triazole-5-carbonitrile (6). The physical constants of these compounds are recorded and discussed. The protonation of 4-amino-2-methyl-1,2,3-triazoles is unusual, taking place on the primary amino-group.

A SET of 4-amino-1,2,3-triazole-5-carbaldehydes (1a—d), required for the synthesis of *N*-alkylated *v*-triazolo[4,5-*d*]pyrimidines (' 8-azapurines ') of interest in anti-cancer research, could not be obtained from the related 4-aminotriazole-5-carbonitriles (available from recent work [1-3]) by the standard methods for converting nitriles into aldehydes. For example, the Stephen reaction [4] gave only polymers of the expected products (which are acid-sensitive), and metal hydrides (such as lithium aluminium hydride) failed to react because of complex formation. Equally unsuccessful were the three Backeberg–Staskun reactions [5] based on Raney nickel.

† In this paper, the amino-group of aminotriazoles is consistently numbered **4**, to facilitate comparisons.

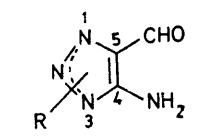
[1] A. Albert, *J. Chem. Soc.* (*C*), 1970, 230.
[2] A. Albert, *J. Chem. Soc.* (*C*), 1969, 2379.
[3] A. Albert, *Chem. Comm.*, 1970, 858.
[4] H. Stephen, *J. Chem. Soc.*, 1925, **127**, 1874.
[5] O. G. Backeberg and B. Staskun, *J. Chem. Soc.*, 1962, 3961; T. van Es and B. Staskun, *J. Chem. Soc.*, 1965, 5775; B. Staskun and O. G. Backeberg, *J. Chem. Soc.*, 1964, 5880.

Catalytic hydrogenation of 4-amino-2-methyl-1,2,3-triazole-5-carbonitrile in the presence of aldehyde-trapping reagents [6] was then tried, and gave the phenylhydrazone, the phenylsemicarbazone, and the azine of 4-amino-2-methyl-1,2,3-triazole-5-carbaldehyde. However, the free aldehyde could not be liberated by (*a*) a large excess of another aldehyde, (*b*) a concentration of acid too weak to polymerize the products, or (*c*) oxidation with lead tetra-acetate,[7] chromyl acetate,[8] or (for the azine) periodic acid.[9]

Finally the required amino-aldehydes (1a—d) were produced from the corresponding nitriles by hydrogenation over palladium in hydrochloric acid of such a strength (found by trial to be 0·1M) that the initially

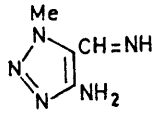
[6] H. Plieninger and G. Werst, *Ber.*, 1955, **88**, 1956; J. Davoll and A. M. Johnson, *J. Chem. Soc.* (*C*), 1970, 997.
[7] S. L. Lee, G. B. Gubelt, A. M. Cameron, and J. Warkentin, *Chem. Comm.*, 1970, 1074.
[8] H. Schildknecht and G. Hatzmann, *Angew. Chem. Internat. Edn.*, 1968, **7**, 293.
[9] A. J. Fatiadi, *Chem. and Ind.*, 1971, 64.

formed imine, *e.g.* (2), was hydrolysed faster than the resulting amino-aldehyde was polymerized. The yields ranged from 45 to 92%. In the absence of acid, the imine was reduced faster than the nitrile, leading to

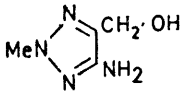


(1)

a; R = 1-Me
b; R = 2-Me
c; R = 3-Me
d; R = 3-CH_2Ph



(2)



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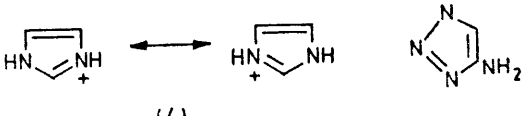

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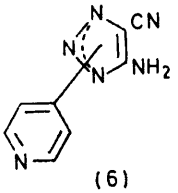
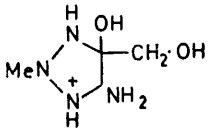


(6)



(7)

(*a*) the 5-aminomethyl analogue and (*b*) the secondary amine formed from this and the imine.[3] This method for obtaining aldehydes from nitriles by hydrogenation seems to have been used, in heterocyclic chemistry, only for 4-amino-5-cyanopyrimidines.[10]

The amino-aldehydes (1) were obtained from 4-amino-1,2,3-triazole-5-carboxamides also, by a route similar to that[11] used to convert 2-aminopyrazine-3-carboxamide into 2-aminopyrazine-3-carbaldehyde. For example, 4-amino-2-methyl-1,2,3-triazole-5-carboxylic acid, obtained from the corresponding 5-carboxamide by alkaline hydrolysis,[12] was esterified in methanol–sulphuric acid, and the methyl ester (obtained in excellent yield) was reduced to the hydroxymethyl analogue (3) with lithium aluminium hydride; finally this primary alcohol was oxidized to the aldehyde with manganese dioxide. Also 4-amino-3-benzyl-1,2,3-triazole-5-carbaldehyde was obtained by this method (in 55% overall yield) from the 5-ethoxycarbonyl derivative, prepared directly by the reaction[13] of benzyl azide with ethyl cyanoacetate. For making small amounts of the amino-aldehydes, the hydrogenation method was found preferable because of the smaller number of steps and the ready accessibility of the starting materials (nitriles) from the amides. However, the necessarily high proportion of solvent to substrate during hydrogenation made the oxidative method preferable for larger scale work.

The amino-aldehydes showed strong i.r. absorption around 1650—1680 cm^{-1} (C=O stretching) comparable to that of 2-aminopyrazine-3-carbaldehyde.[11] The ^1H n.m.r. spectra showed a sharp singlet at τ −0·1 to +0·1 (CHO). The aldehydes were stable at room temperature both in the solid state and dissolved in 0·1N-hydrochloric acid; but in N-acid, they were almost completely polymerized after a month (at 20—25°).

4-Amino-1-methyl-1,2,3-triazole (5) was made, by decarboxylating the 5-carboxylic acid, in order to compare its pK_a value (found to be 2·42) with that of 4-amino-3-methyl-1,2,3-triazole[2] (2·27), which had been thought to be unusually low. Attempted preparation of 4-amino-2-methyl-1,2,3-triazole by similar decarboxylation[1,2,14] under various conditions led to either decomposition or the recovery of the carboxylic acid.

4-Amino-1,2,3-triazole-5-carbonitrile was prepared by modifying the method of Hoover and Day[13] which seems to be insufficiently described. The acidic pK_a value was 6·15, which is, as expected, lower than those of the 5-carbamoyl[12] (7·79) and the 5-(methylthio)carbonyl[2] (7·12) analogues. An attempted synthesis of the nitrile by dehydrating 4-amino-1,2,3-triazole-5-carboxamide with thionyl chloride in pyridine gave an unexpected product, of empirical formula $(C_4H_3N_3)_n$. The n.m.r. spectrum had peaks typical of a 4-substituted pyridine [τ 1·11 (2H, q, J 5·5 and 1 Hz) and 2·05 (2H, q, J 5·5 and 1 Hz)] and the i.r. spectrum showed a sharp absorption at 2240 cm^{-1} (CN). These data indicated that the compound was 4-amino-2-(1- or 3-)(4-pyridyl)-1,2,3-triazole-5-carbonitrile (6). Although the position of the pyridyl group was uncertain, the 2-position seemed most likely, because paper chromatography of the product in aqueous ammonium chloride and in butanol–5N-acetic acid produced a *fluorescent* spot, which is characteristic of a 2-substituted 1,2,3-triazole.[12]

When 4-amino-1,2,3-triazole-5-carbonitrile was hydrogenated as for the *N*-substituted derivatives, the product was so unstable that it was not further pursued.

Ionization constants and u.v. spectra of 4-amino-1,2,3-triazoles are shown in Table 1. The normal small bathochromic shift (about 20 nm for the longer wavelength peak), with slight decrease of intensity, was observed when any of the 1- or 3-substituted 4-amino-1,2,3-triazoles was converted into its cation (for other examples of this behaviour in 1,2,3-triazoles, see refs. 1, 2, and 13). The lack of a hypsochromic shift and the

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[11] A. Albert and K. Ohta, *J. Chem. Soc.* (*C*), 1971, 2357.

[12] A. Albert, *J. Chem. Soc.* (*C*), 1968, 2076.

[13] J. R. E. Hoover and A. R. Day, *J. Amer. Chem. Soc.*, 1956, **78**, 5832.

[14] N. J. Cusack, G. Shaw, and G. J. Litchfield, *J. Chem. Soc.* (*C*), 1971, 1501; T. Cohen and R. A. Schambach, *J. Amer. Chem. Soc.*, 1970, **92**, 3189; B. Frydman, S. J. Reil, J. Boned and H. Rapoport, *J. Org. Chem.*, 1968, **33**, 3762; S. Nawa· S. Matsuura, and Y. Hirata, *J. Amer. Chem. Soc.*, 1953, **75**, 4450·

similarity of the pK_a value of 4-amino-3-benzyl-5-hydroxymethyl-1,2,3-triazole (1·15) to that of 1-methyl-1,2,3-triazole [15] (pK_a 1·25) suggested that the protonation took place on a ring nitrogen atom and involved the imidazolium type (4) of resonance stabilization.[16]

wavelength peak had to be excluded: (*a*) hydration across the 1,5-double bond followed by protonation on N-3, in an isolated amidino-group, and (*b*) hydration across the 3,4-double bond followed by protonation on the carbinolamine group. The n.m.r. spectra of 4-amino-3-benzyl-(and 2-methyl-)5-hydroxymethyl-1,2,3-triazoles in four solvents are shown in Table 2. The

TABLE 1

Ionization constants and u.v. spectra

Species [a]		Ionization in water (20°) pK_a	Spread (±)	Concn. (M)	A.w.l.[b] (nm)	Spectroscopy in water $\lambda_{max.}$/nm	log ε	pH [c]
4-Amino-1,2,3-triazole-5-carbaldehyde								
1-Methyl- (1a)	0 [d]					243, 316	3·64, 3·83	3
2-Methyl-	0					236, 302	3·60, 3·79	2
	+	−0·80	0·03	$2·79 \times 10^{-5}$	300	241	3·90	−4
3-Methyl-	0					237, 287	3·60, 3·96	2
	+	−1·54	0·05	$2·14 \times 10^{-5}$	275	241, 301	3·67, 3·91	−4
4-Amino-5-hydroxymethyl-1,2,3-triazole								
2-Methyl- (3)	0					~210, 252	~3·43, 3·76	4
	+	1·56	0·03	$1·58 \times 10^{-4}$	250	220,[f]	3·81	−2
3-Benzyl-	0					246	3·74	4
	+	1·15	0·04	$1·09 \times 10^{-4}$	265	265	3·73	−2
4-Amino-1-methyl-1,2,3-triazole (5)								
	0					241	3·49	5
	+	2·42	0·02	$2·16 \times 10^{-4}$	245	262	3·17	0
4-Amino-1,2,3-triazole-5-carbonitrile								
	0					251	3·77	3
	−	6·15 [e]	0·03	$1·23 \times 10^{-4}$	230	252	3·79	9
4-Amino-5-cyano-2-(1- or 3-)(4-pyridyl)-1,2,3-triazole (6)	0					225, 319	4·21 4·22	7
	+	4·00	0·02	$4·08 \times 10^{-5}$	350	244, 351	4·13, 4·28	1

[a] Neutral species (0), cation (+), anion (−). [b] Analytical wavelength for spectrometric determinations. [c] Negative values are H_0 for solutions in sulphuric acid (K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1959, 1096). [d] A basic pK_a value (<1) could not be measured because of sensitivity of cation to acid. [e] Acidic constants, all others are basic. [f] *Cf.* $\lambda_{max.}$ 218 nm (log ε 3·79) for 2-methyl-1,2,3-triazole (neutral species), not previously determined.

The cations of 4-amino-2-methyl-1,2,3-triazoles (Table 1) lacked the long wavelength band seen in the neutral species (a similar lack of absorption was found for 4-amino-2-methyl-1,2,3-triazole-5-carboxamide [12]). Solutions of these cations gave, when neutralized, spectra identical with those of the neutral species, confirming that no acid-induced decomposition had occurred. That 4-amino-5-hydroxymethyl-2-methyl-1,2,3-triazole is basic (whereas 2-methyl-1,2,3-triazole lacks basic properties [16]) indicates that it becomes protonated on the exocyclic nitrogen atom, a result not previously reported for an α-amino nitrogen heterocycle, but likely to happen when amidinium resonance cannot occur, because of an unfavourable distribution of electrons. In these circumstances, the primary amino-group, weakly basic as it is, can gain the proton. The loss of the long wavelength peak on passing from neutral species to cation is typical of the behaviour of aromatic primary amino-groups.[17] Thus the spectrum of the cation of aniline is almost identical with that of benzene, and the spectrum of the cation of 4-amino-5-hydroxymethyl-2-methyl-1,2,3-triazole is almost identical with that of 2-methyl-1,2,3-triazole (neutral species (see Table 1).

Two alternative explanations for the loss of the long

TABLE 2

^1H N.m.r. spectra of 4-amino-5-hydroxymethyl-1,2,3-triazoles at 33°

	τ Values CH_2·OH	CH_2Ph	Ph	Me	Solvent [b]
3-Benzyl	5·58	4·66	2·70		A
	a	4·42	2·43		B
	5·19	4·35	2·48		C
	4·88	4·33	2·50		D
2-Methyl	5·54			6·19	A
	5·35			6·00	B
	5·15			5·78	C
	5·09			6·10	D

[a] Overlapped by the HOD peak. [b] A, [$^2H_6$]dimethyl sulphoxide; B, deuterium oxide; C, 10N-deuteriochloric acid; D, anhydrous trifluoroacetic acid.

chemical shift of the methylene proton of the 2-methyltriazole changed no more, with change in solvent, than that of the methyl proton or of the hydroxymethylene proton of the 3-benzyl derivative, whereas an upfield shift would be expected on converting an allylic into an aliphatic proton upon forming the cation (7). This fact

[15] A. Albert in ' Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York, 1963, **1**, 1.
[16] C. Pedersen, *Acta Chem. Scand.*, 1959, **13**, 888.
[17] C. L. Harberts, P. M. Heertjes, L. J. N. van der Hulst, and H. I. Waterman, *Bull. Soc. chim. France*, 1936, **3**, 643.

excluded possibility (*a*). Possibility (*b*) seemed unlikely because of the stability of the cation in acid solution. Finally, both possibilities were excluded by measuring the basic pK_a value of 4-amino-5-hydroxymethyl-2-methyl-1,2,3-triazole in rapid-reaction apparatus,[18] by rapid acidification of a neutral solution containing the neutral species. The value obtained (*1·57 ± 0·03*), being similar to that given by the usual slow equilibrium method (1·56; see Table 1), indicated that no covalent hydration had taken place when forming the cation.

EXPERIMENTAL

U.v. spectra were measured with a Unicam SP 800 spectrophotometer; the wavelength and intensity of each maximum were then checked with a Unicam SP 500 (series 2) manual instrument. ^{1}H N.m.r. spectra were determined with a Perkin-Elmer R10 instrument operating at 33·3° and 60 MHz, with tetramethylsilane or sodium 3-trimethylsilylpropane-1-sulphonate as internal standard. The presence of an NH or OH group was confirmed by exchange with D_2O. I.r. spectra were taken with a Unicam SP 200 spectrometer calibrated with polystyrene at 1603 cm^{-1} (for mulls in Nujol). Yields for substances without sharp m.p. refer to material giving only one spot on paper chromatograms run in (*a*) aqueous 3% ammonium chloride and (*b*) butanol–5N-acetic acid. Identity of compounds prepared by different routes was established by m.p., i.r. spectral, and paper chromatographic comparisons. Ionization constants were determined for solutions in water (10^{-4}M) as in ref. 19.

4-Amino-2-methyl-1,2,3-triazole-5-carbaldehyde Phenylhydrazone, Phenylsemicarbazone, and Azine.—A mixture of 4-amino-2-methyl-1,2,3-triazole-5-carbonitrile [3] (0·25 g, 0·002 mol) and phenylhydrazine (0·26 g, 0·0024 mol) in 50% acetic acid (20 ml) was hydrogenated over Raney nickel until 0·0024 mol of hydrogen had been absorbed. The mixture was filtered hot and the filtrate taken to dryness *in vacuo*. Addition of water (5 ml) to the residue gave a precipitate which, recrystallized from ethanol (15 parts), gave *4-amino-2-methyl-1,2,3-triazole-5-carbaldehyde phenylhydrazone* (65%), m.p. 182·5° [Found (material dried at 110° and 0·05 mmHg): C, 55·6; H, 5·4; N, 39·3. $C_{10}H_{12}N_6$ requires C, 55·5; H, 5·6; N, 38·9%], $\nu_{max.}$ 3440w (NH), 3330m (NH), 3270m (NH), 3150w, 3050w—2950w (NMe), 1625m, 1600s (NH and Ph), 1560s (N=N), 1505s, 1300m, and 1265s cm^{-1}, τ [$(CD_3)_2SO$] 5·99 (3H, s, NMe), 4·40br (2H, s, NH_2), 2·4—3·4 (6H, NH and Ph), and 1·76 (1H, s, CH=N). This material was identical with a specimen prepared by condensing 4-amino-2-methyl-1,2,3-triazole-5-carbaldehyde (see later) with phenylhydrazine in 50% acetic acid.

The nitrile and 4-phenylsemicarbazide (0·36 g, 0·0024 mol) were similarly hydrogenated; the mixture was filtered and taken to dryness. A chloroform extract of the residue was washed (saturated aqueous $NaHCO_3$), dried (Na_2SO_4), and evaporated. The residue was recrystallized from 95% ethanol (20 parts) to give the *phenylsemicarbazone* (67%), m.p. 183—184° [Found (material dried at 110° and 0·05 mmHg): C, 50·8; H, 5·2; N, 37·7. $C_{11}H_{13}N_7O$ requires C, 50·95; H, 5·05; N, 37·8%], $\nu_{max.}$ 3450w, 3300m, 3230m (NH), 2960w, 1670s (C=O str), 1635m (C=N), 1605m, 1540s, 1460m, and 765 cm^{-1}, τ [$(CD_3)_2SO$] 6·01 (3H, s, NMe), 4·10br (2H, NH_2), 2·05—3·00 (5H, s, Ph), 1·71 (1H, s, CH=N), 0·83 (1H, s, NH), and −0·60 (1H, s, NH).

The nitrile (0·37 g) and hydrazine hydrate (0·18 g, 0·0036 mol) were similarly hydrogenated. Ethanol (100 ml) was added and the mixture was filtered at 70°. The filtrate was taken to dryness *in vacuo*, and the residue, recrystallized from ethanol (500 parts), gave the *azine* (0·25 g, 66%), m.p. 256—257° [Found (material dried at 110° and 0·05 mmHg): C, 38·85; H, 5·0; N, 56·0. $C_8H_{12}N_{10}$ requires C, 38·7; H, 4·9; N, 56·4%], $\nu_{max.}$ 3450m, 3300m (NH), 2950w (NMe), 1635s (C=N), 1610m, 1550m, 1400m, and 1360m cm^{-1}, τ [$(CD_3)_2SO$] 5·91 (s, NMe), 3·92br (s, NH_2), and 0·97 (s, CH=N) (integral ratio 3 : 2 : 1).

4-Amino-1-(2- and 3-)methyl-1,2,3-triazole-5-carbaldehydes (1a—c).—The appropriate 5-cyano-derivative [2,3] (0·12 g, 0·001 mol) in 0·1N-hydrochloric acid (60 ml) was hydrogenated at 20° and atmospheric pressure over 10% Pd–C until 0·001 mol of hydrogen had been absorbed. The catalyst was filtered off and the filtrate, neutralized with potassium hydrogen carbonate, was extracted with chloroform (3 × 50 ml; continuous extraction was necessary for the 3-methyl isomer). The extract was dried (Na_2SO_4) and the solvent evaporated *in vacuo* to give the following compounds: *4-amino-1-methyl-1,2,3-triazole-5-carbaldehyde* (1a) (45%), m.p. 135° (from 60 parts of benzene) [Found (for material sublimed at 80° and 0·05 mmHg): C, 38·0; H, 4·9; N, 44·7. $C_4H_6N_4O$ requires C, 38·1; H, 4·8; N, 44·4%], $\nu_{max.}$ 3440w, 3300m, 3200w, 1660s (C=O str), 1635m, 1552m, 1410m, 1330m, 1180m, and 780m cm^{-1}, τ [$(CD_3)_2SO$] 5·89 (3H, s, NMe), 3·70br (2H, NH_2), and 0·10 (1H, s, CHO); *4-amino-2-methyl-1,2,3-triazole-5-carbaldehyde* (1b) (54%), m.p. 102—103° (from 10 parts of benzene) [Found (material dried at 25° and 0·1 mmHg): C, 37·9; H, 4·8; N, 44·2%], $\nu_{max.}$ 3470w, 3340m (NH), 3230w (NH), 2960w (Me), 2830w (CHO str.), 1680s (C=O str.), 1630s, 1550m, and 780m cm^{-1}, τ [$(CD_3)_2SO$] 5·89 (3H, s, NMe), 3·84br (2H, NH_2), and −0·09 (1H, s, CHO); and *4-amino-3-methyl-1,2,3-triazole-5-carbaldehyde* (1c) (68%), m.p. 182·5° (de comp.) (from 80 parts of ethyl acetate) [Found (material dried at 65° and 0·1 mmHg): C, 38·0; H, 4·9; N, 44·2%], $\nu_{max.}$ 3440w, 3370w, 3280w, 3220w (NH), 1650br,s (C=O str.), 1570m, 1530m, 1360m, 1315m, and 820m cm^{-1}, τ [$(CD_3)_2SO$] 6·23 (3H, s, NMe), 3·02br (2H, NH_2), and 0·12 (1H, s, CHO).

4-Amino-3-benzyl-1,2,3-triazole-5-carbaldehyde (1d).—4-Amino-3-benzyl-1,2,3-triazole-5-carbonitrile [1] (1·99 g, 0·01 mol) in ethanol (200 ml) and 0·2N-hydrochloric acid (300 ml) was hydrogenated similarly. The catalyst was filtered off and the filtrate was neutralized with potassium hydrogen carbonate, to 150 ml, and refrigerated. The deposited crystals, recrystallized from benzene (140 parts), gave the *aldehyde* (1d) (92%), m.p. 169° [Found (material dried at 65° and 0·05 mmHg): C, 59·7; H, 4·7; N, 27·6. $C_{10}H_{10}N_4O$ requires C, 59·4; H, 5·0; N, 27·7%], $\nu_{max.}$ 3430w, 3340w, 3250w, 3200w (NH), 1670s (C=O str.), 1635m, 1575m, and 840m cm^{-1}, τ [$(CD_3)_2SO$] 4·54 (2H, s, CH_2Ph), 2·85br (2H, s, NH_2), 2·68 (5H, s, Ph), and 0·10 (1H, s, CHO).

Methyl 4-Amino-2-methyl-1,2,3-triazole-5-carboxylate.—To a solution of 4-amino-2-methyl-1,2,3-triazole-5-carboxylic acid [12] (5·82 g, 0·041 mol) in absolute methanol (250 ml), cooled to 0°, was added concentrated sulphuric acid (5 ml). The mixture was heated under reflux for 7 h, cooled, neutralized with sodium hydrogen carbonate, and filtered. The filtrate was taken to dryness *in vacuo* and the residue extracted with chloroform (200 ml). The extract, taken to

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dryness and recrystallized from benzene (7 parts), gave the *ester* (91%), m.p. 103—104° [Found (material dried at 65° and 0·05 mmHg): C, 38·6; H, 5·4; N, 35·7. $C_5H_8N_4O_2$ requires C, 38·5; H, 5·2; N, 35·9%], $\nu_{max.}$ 3500m (NH), 3360m (NH), 1700s (C=O str.), 1615s, 1555m, 1520m, 1310m, 1195m, and 1145s (C–O) cm^{-1}, τ ($CDCl_3$) 6·00 (3H, s, OMe), 5·87 (3H, s, NMe), and 5·10br (2H, NH_2).

4-Amino-5-hydroxymethyl-2-methyl-1,2,3-triazole (3).—A solution of methyl 4-amino-2-methyl-1,2,3-triazole-5-carboxylate (2·00 g, 0·013 mol) in tetrahydrofuran (70 ml) and diethyl ether (500 ml) was added to a suspension of lithium aluminium hydride (1·09 g, 0·026 mol) in diethyl ether (200 ml) at room temperature with stirring; stirring was continued for 6 h more. Water (5 ml) was cautiously added, still with stirring, and the inorganic substances were filtered off. The filtrate, dried over potassium carbonate, was taken to dryness. The residue, sublimed at 110° and 0·1 mmHg, and recrystallized from a mixture of ethanol and light petroleum (60—80°), gave the *alcohol* (3) (60%), m.p. 78—79° [Found (material dried at 25° and 0·1 mmHg): C, 37·5; H, 6·5; N, 43·3. $C_4H_8N_4O$ requires C, 37·5; H, 6·3; N, 43·7%], $\nu_{max.}$ 3400m, 3350s, 3250s, 2950w (NMe), 2900w (NMe), 1650m, 1555m, and 1010s (C–O) cm^{-1}, τ [$(CD_3)_2SO$] 6·09 (3H, s, NMe), 5·55 (2H, d, J 6 Hz, CH_2·O), 5·11 (2H, NH_2), and 5·01 (1H, t, J 6 Hz, OH) (the peaks at τ 5·11 and 5·01 disappeared and that at τ 5·55 changed to a singlet when D_2O was added).

4-Amino-3-benzyl-5-hydroxymethyl-1,2,3-triazole.— Ethyl 4-amino-3-benzyl-1,2,3-triazole-5-carboxylate [13] (0·50 g, 0·0021 mol) in tetrahydrofuran (100 ml) was treated similarly with lithium aluminium hydride (0·21 g, 0·005 mol); the mixture was finally heated under reflux for 2 h, then worked up similarly. The residue, recrystallized from ethyl acetate (80 parts), gave the *alcohol* (0·29 g, 70%), m.p. 147° [Found (material dried at 65° and 0·05 mmHg): C, 58·8; H, 5·8; N, 27·4. $C_{10}H_{12}N_4O$ requires C, 58·8; H, 5·9; N, 27·4%], $\nu_{max.}$ 3340s, 3210s, 1685s, 1600s, 1250m, and 1030s cm^{-1}, τ [$(CD_3)_2SO$] 5·58 (2H, d, J 6 Hz, CH_2·O), 5·27 (1H, t, J 6 Hz, OH), 4·66 (2H, s, CH_2Ph), 4·58br (2H, s, NH_2), and 2·70 (5H, s, Ph) (addition of D_2O removed the signals at τ 5·27 and 4·58, and the doublet at τ 5·58 collapsed to a singlet).

Oxidation of Hydroxymethyl Derivatives.—To a solution of 4-amino-5-hydroxymethyl-2-methyl-1,2,3-triazole (0·57 g, 0·0045 mol) in chloroform (100 ml) was added manganese dioxide (5·5 g, 0·045 mol) at room temperature with stirring, and stirring was continued for 2·5 h more. The mixture was filtered and the filtrate taken to dryness *in vacuo*. The residue, recrystallized from benzene (10 parts), gave 4-amino-2-methyl-1,2,3-triazole-5-carbaldehyde (1b) (71%). 4-Amino-3-benzyl-5-hydroxymethyl-1,2,3-triazole (0·061 g, 0·0003 mol), similarly oxidized with manganese dioxide (0·037 g, 0·003 mol) in chloroform (35 ml), gave 78% of the aldehyde (1d).

4-Amino-1-methyl-1,2,3-triazole (5).—4-Amino-1-methyl-1,2,3-triazole-5-carboxylic acid [20] (0·50 g, 0·0035 mol) was heated at 210° (bath temp.) for 15 min under nitrogen. The cooled melt was dissolved in chloroform, then passed through an alumina (5 g) column developed with chloroform. The solution was taken to dryness and the residue, recrystallized from benzene (90 parts), gave 4-amino-1-methyl-1,2,3-triazole (83%), m.p. 88—89° (lit.,[16] 88—89°); τ [$(CD_3)_2SO$] 6·13 (3H, s, NMe), 5·37br (2H, NH_2), and 2·91 (1H, s, CH).

4-Amino-1,2,3-triazole-5-carbonitrile.— 4-Amino-3-benzyl-1,2,3-triazole-5-carbonitrile [1] (7·25 g, 0·036 mol) was added to liquid ammonia (200 ml) with stirring. Pieces of sodium (2·01 g, 0·086 mol) were slowly added during 1 h and stirring was continued until the red colour disappeared. Ammonium chloride (5·84 g, 0·09 mol) was added cautiously and the mixture was kept at room temperature overnight and taken to dryness *in vacuo*. The residue was extracted with diethyl ether (300 ml) (Soxhlet). The extract was evaporated and the residue, extracted with N-NaOH, liberated at pH 1·5, and recrystallised from water (10 parts), gave 4-amino-1,2,3-triazole-5-carbonitrile (78%), m.p. indefinite (lit.,[13] 226—228°; *ca.* 50% yield) [Found (material dried at 110° and 0·05 mmHg): C, 33·1; H, 3·05; N, 64·4%; M^+ 109. Calc. for $C_3H_3N_5$: C, 33·0; H, 2·8; N, 64·2%; M, 109], $\nu_{max.}$ 3450m, 3400m, 3320m, and 3250s (NH), 2240m (sharp, C≡N str.), 1660s, and 1605m cm^{-1}.

Reaction of 4-Amino-1,2,3-triazole-5-carboxamide with Thionyl Chloride in Pyridine.—To a mixture of 4-amino-1,2,3-triazole-5-carboxamide [13] (4·9 g, 0·039 mol) and anhydrous pyridine (60 ml) was slowly added thionyl chloride (12 ml, 0·16 mol) at 3—5°. The mixture was stirred at 25° for 8 h and poured on ice (200 g). The suspension, refrigerated overnight, deposited a precipitate which, after drying ($CaCl_2$) at room temperature, was continuously extracted with diethyl ether (250 ml) (Soxhlet). Material from the extract, recrystallized from ethanol (100 parts), gave *4-amino-2-(1- or 3-)(4-pyridyl)-1,2,3-triazole-5-carbonitrile* (6) (24·5%), m.p. 236° (decomp.) [Found (material dried at 110° and 0·1 mmHg): C, 51·9; H, 3·1; N, 45·8. $C_8H_6N_6$ requires C, 51·6; H, 3·25; N, 45·1%], $\nu_{max.}$ 3480m (NH), 3390w (NH), 3150m (NH), 2240w (CN), 1660s, 1575s, 1330s, 950m, and 825m cm^{-1}.

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