Studies on the Azidoazomethine–Tetrazole Equilibrium. I. 2-Azidopyrimidines[1]

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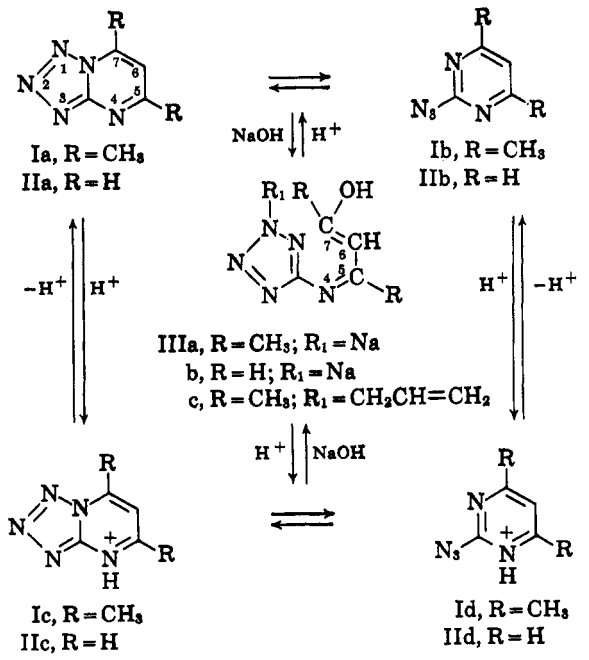
The azidoazomethine–tetrazole equilibrium for two similar pyrimidine derivatives (I and II) has been examined by means of infrared and proton magnetic resonance spectrometry. Only the 5,7-dimethyltetrazolo[1,5-*a*]pyrimidine tautomer (Ia) can be detected in the solid state and in a dimethyl sulfoxide-d_6 solution of I. When I is dissolved in trifluoroacetic acid, however, only the azido form (Ib and Id) can be detected. In other solvents both the azido and tetrazolo tautomers can be identified and for these solutions an equilibrium constant, K_T, can be calculated from the ratio of the amount of the azido tautomer to that of the tetrazolo tautomers. In general the value of K_T is greatest in nonpolar solvent, and in deuteriochloroform was found to increase with temperature; the heat of tautomerization of Ia to Ib is found to be $+6.8 \pm 0.5$ kcal. mole^{-1}. Furthermore, the equilibrium between tetrazolo[1,5-*a*]pyrimidine (IIa) and 2-azidopyrimidine (IIb) is independent of concentration in dimethyl sulfoxide-d_6. Comparison of the equilibrium involving I with that involving II indicates that tetrazole destabilization in I is less, which is attributed to the electron release of the methyl groups. In addition, a study of the ultraviolet spectra of I in aqueous sodium hydroxide shows the existence of a second equilibrium—between Ia and the ring-opened tetrazole IIIa.

Treatment of 5-aminotetrazole with acetylacetone[2a] and reaction of 4,6-dimethyl-2-hydrazinopyrimidine with nitrous acid[2a,b] has been reported to give the same product, 5,7-dimethyltetrazolo[1,5-*a*]pyrimidine (Ia).[3] Presumably the conjugated tetrazole IIIa is an intermediate in the first reaction, and 2-azido-4,6-dimethylpyrimidine (Ib) is probably an intermediate in the second. The transparency of the solid-state infrared spectrum of I[4] in the azido absorption region (2160–2120 cm.$^{-1}$)[5] provides support for the assigned tetrazolo[1,5-*a*]pyrimidine structure. Previously the 54-mμ bathochromic shift in the maximum of the ultraviolet spectrum of a basic solution of I from that of a neutral solution of I was explained in terms of "dipolar ions."[6] This explanation is now rejected. From a study of the ultraviolet, infrared, and proton magnetic resonance spectra we have found that I is actually involved in two different equilibria. One equilibrium is between Ia and Ib and the second between I and IIIa.[7]



Existence of an azidoazomethine–tetrazole equilibrium has been demonstrated for several heterocyclic systems.[8] Heretofore the cause for destabilization of the more stable tetrazole tautomer in fused-ring tetrazoles has been attributed to electron withdrawal, which also results in stabilization of the electron-donating azido group.[8a-c] During our investigation of this equilibrium we have also found solvent and temperature effects similar to those observed by Sheinker, *et al.*,[8d] for the azidoazomethine–tetrazole equilibrium in the compound obtained from 2-chloro- or 2-hydrazinobenzothiazole. In other related investigations Henry, *et al.*, reported on the thermal isomerization of substituted 5-aminotetrazoles for which a substituted guanyl azide intermediate is proposed,[9] whereas Boyer, *et al.*, suggested, but did not establish, that the effect of solvents on the azidoazomethine–tetrazole equilibrium in the case of pyridotetrazole determined the course of the reduction of this compound.[10]

Azido absorption is absent in the infrared spectrum[4] of a N,N-dimethylformamide solution of I, but is present at 2180 cm.$^{-1}$ in the spectrum of a trifluoroacetic acid solution. Presumably the major form in these solutions is in equilibrium with the other tautomer. However, in the p.m.r. spectra of I only the tetrazolo form Ia is detected in dimethyl sulfoxide-d_6 and only the

(1) This investigation was supported by funds from the C. F. Kettering Foundation and the Cancer Chemotherapy National Service Center, National Cancer Institutes, National Institutes of Health, Contract No. PH-43-64-51. A preliminary report of part of this work has appeared: C. Temple, Jr., and J. A. Montgomery, *J. Am. Chem. Soc.*, **86**, 2946 (1964).

(2) (a) C. Bulow, *Chem. Ber.*, **42**, 4433 (1909); (b) R. Giuliano and G. Leonardi, *Farmaco* (Pavia), *Ed. sci.*, **11**, 389 (1956); (c) K. Shirakawa, Japanese Patent 777 (Feb. 6, 1957); *Chem. Abstr.*, **52**, 4699*h* (1958).

(3) A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," American Chemical Society, Washington, D. C., 1960. For a different numbering system, see A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940.

(4) The infrared spectra were determined in pressed potassium bromide disks or, when indicated, as a contact film or solution, with a Perkin-Elmer Model 221-G spectrophotometer. The infrared spectrum of the trifluoroacetic acid solution was determined in an Irtran-2, fixed-thickness cell. The ultraviolet spectra were determined with a Cary Model 14 recording spectrophotometer.

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 1st Ed., John Wiley and Sons, Inc., New York, N. Y., 1954, p. 223.

(6) F. C. Nachod and E. A. Steck, *J. Am. Chem. Soc.*, **70**, 2819 (1948).

(7) That other tautomers of IIIa and IIIb may exist is recognized.

(8) (a) J. H. Boyer and E. J. Miller, Jr., *J. Am. Chem. Soc.*, **81**, 4671 (1959); (b) J. H. Boyer and H. W. Hyde, *J. Org. Chem.*, **25**, 458 (1960); (c) C. Temple, Jr., R. L. McKee, and J. A. Montgomery, *J. Org. Chem.*, **27**, 1671 (1962); (d) Y. N. Sheinker, I. Ya. Postovskii, N. P. Bednyagina, L. B. Senyavina, and L. F. Lipatova, *Dokl. Akad. Nauk. SSSR*, **141**, 1388 (1961); (e) Ya. Postovskii and I. N. Goncharova, *Zh. Obsch. Khim.*, **33**, 2334 (1963).

(9) (a) R. A. Henry, W. G. Finnegan, and E. Lieber, *J. Am. Chem. Soc.*, **76**, 88 (1954); (b) *ibid.*, **77**, 2264 (1955).

(10) J. H. Boyer, M. S. Chang, and R. F. Reinisch, *J. Org. Chem.*, **25**, 286 (1960).

TABLE I

EQUILIBRIUM CONSTANTS AND P.M.R SPECTRAL ASSIGNMENTS[a]

Solvent	% concn. (w./v.)	K_T[d,f]	τ-value (multiplicity) (J in c.p.s.)[b] Tetrazolo[1,5-a]pyrimidine (Ia) 5-CH_3	7-CH_3	6-H	Azidopyrimidine (Ib) 4(6)-CH_3	5-H
DMSO-d_6[c]	5	g	7.31 (s)	7.11 (d) (1.00)	2.62 (q)		
TFAA[c]	10	g				7.23 (d) (0.55)	2.65 (m)
Pyridine	5	0.14	7.43 (s)	7.25 (d) (1.00)	h	7.72 (d) (0.50)	h
$CDCl_3$	7	0.36	7.22 (s)	7.00 (d) (1.10)	2.92 (q)	7.53 (d) (0.50)	3.15 (m)
Acetone-d_6	5	0.08	7.28 (s)	7.03 (d) (0.90)	2.65 (q)	7.58 (d) (0.55)	2.95 (m)
CD_3OD	4	0.12	7.24 (m)	7.02 (m)	2.67 (s)	7.55 (m)	2.99 (s)

Solvent	% concn. (w./v.)	K_T[e,f]	Tetrazolo[1,5-a]pyrimidine (IIa) 5-H	7-H	6-H	Azidopyrimidine (IIb) 4(6)-H	5-H
DMSO-d_6[c]	32	0.07	0.70 (q) (J_{56} = 4.1)(J_{57} = 1.8)	0.15 (q) (J_{67} = 7.0)	2.23 (q)	1.18 (d) (5.0)	2.57 (t)
TFAA[c]	10	g				0.95 (d) (5.0)	2.30 (t)
$CDCl_3$	<5	g				1.40 (d) (5.0)	2.97 (t)
Acetone-d_6	<5	0.37	0.82 (q) (J_{56} = 4.1)(J_{57} = 1.8)	0.42 (q) (J_{67} = 7.0)	2.28 (q)	1.28 (d) (5.0)	2.72 (t)

[a] Spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as internal reference. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Precision in J (c.p.s.) for I, ±0.05; for II, ±0.1. [c] DMSO-d_6 = dimethyl sulfoxide-d_6, TFAA = trifluoroacetic acid. [d] Ratio of the integrated intensity of the methyl signal from Ib to the sum of the integrated intensities of the methyl signals from Ia at probe temperature (37–38°). [e] Ratio of the integrated intensity of the 4(6)-proton signal from IIb to the sum of the integrated intensities of the 5- and 7-proton signals from IIa at probe temperature (37–38°). [f] The estimated mean deviation in K_T was less than ±0.02. [g] Only one tautomer was detected. [h] Position uncertain because of solvent interference.

azido form Ib and Id in trifluoroacetic acid (see below). These assignments are substantiated by the characteristic, solvent-independent pattern of the methyl-group bands. In the azido tautomer Ib the methyl groups are equivalent and were found to be involved in long-range coupling with the 5-proton. The methyl groups of the tetrazolo tautomer Ia, however, are nonequivalent and only the less-shielded methyl group, probably in the 7-position, is coupled with the ring proton (see Table I). The p.m.r. spectra show that I in other solutions[11] exists as a tautomeric mixture of the tetrazolo and azido forms (see Figure 1). For each of these solutions an equilibrium constant (K_T) was calculated from the ratio of the integrated intensity of the methyl signal from Ib to the sum of the integrated intensities of the methyl signals from Ia (see Table I). Apparently this is the first instance in which the relative amounts of both the tetrazolo and azido tautomers have been determined.

Undoubtedly protonation of a pyrimidine nitrogen of I occurs in trifluoroacetic acid. The protonation of Ia to give Ic results in electron withdrawal from the tetrazole ring and favors the formation of Id and presumably Ib in which the azido group is electron donating.[12] In contrast, a basic medium (pyridine) has no more effect on tetrazole ring destabilization in Ia than methanol. The equilibrium constant of I has its greatest value in deuteriochloroform, the least polar of the solvents studied. In dimethyl sulfoxide-d_6, the most polar solvent studied, the azido form was not detected, but presumably Ib was present. These results point to the existence of a mobile equilibrium between Ia and Ib, which is dependent upon solvent polarity, and are in good agreement with those obtained by Sheinker, *et al.*, with benzothiazolotetrazole.[8d] In support of this observation, dilution of a 6.8% solution of I in deuteriochloroform to 5.4% with dimethyl sulfoxide-d_6 results in a change of K_T from 0.36 to 0.10. In the remaining

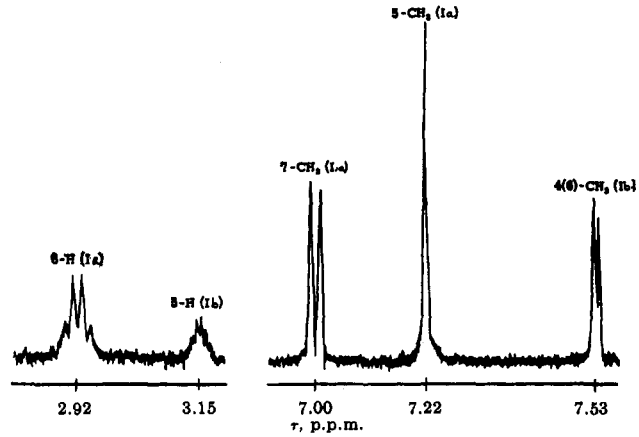


Figure 1.—P.m.r. spectrum of I in deuteriochloroform measured at 60 Mc./sec.$^{-1}$ (7% w./v.).

solvents, however, the value of K_T appears to be less dependent upon solvent polarity. The variation of the equilibrium constant[13] with temperature in deuteriochloroform (see Figure 2) shows that the tautomerization of Ia to Ib is endothermic (ΔH = +6.8 ± 0.5 kcal. mole^{-1}). Log K_T is well correlated with $1/T$ giving a least-squares-derived correlation coefficient of 0.99. The heat of tautomerization of benzothiazolotetrazole to 2-azidobenzothiazole was estimated to be +4.65 in pyridine and +0.98 kcal. mole^{-1} in dioxane by infrared measurements.[8d] Also McEwan and Rigg found that certain simple monocyclic tetrazoles are more stable by 10–12 kcal. than the isomeric noncyclic azides.[14]

Additional information about I is acquired by a study of the parent system itself. The equilibrium between tetrazolo[1,5-a]pyrimidine (IIa) and 2-azidopyrimidine (IIb)[2c] shows that the relative amount of the azido tau-

(11) The infrared spectra of these solutions exhibit azido bands in the 2180–2120-cm.$^{-1}$ region.

(12) Evaporation of the trifluoroacetic acid solution to dryness gave an analytical sample of I, which showed no observable azido absorption in its infrared spectrum.

(13) The equilibrium constants were calculated from p.m.r. spectra determined on a Varian A-60 spectrometer by Dr. Ross G. Pitcher, Varian Associates, Palo Alto, Calif. Each determination was the mean of three runs at the specified temperature, which was verified by the chemical shift difference of the ethylene glycol peaks. The least-squares standard deviation in K_T was less than ±0.01.

(14) W. S. McEwan and M. W. Rigg, *J. Am. Chem. Soc.*, **73**, 4725 (1951).

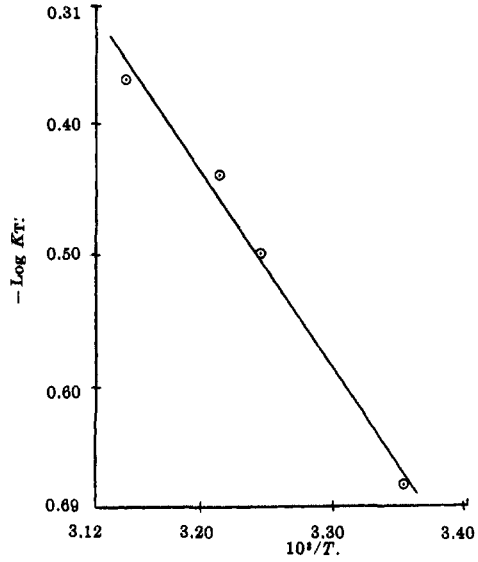


Figure 2.—Effect of temperature on the equilibrium constant (K_T) for I in deuteriochloroform (7% w./v.); K_T[18] = 0.21 (25°), 0.32 (35°), 0.36 (38°), and 0.43 (45°).

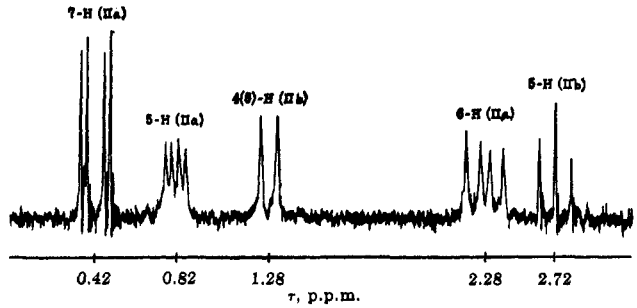


Figure 3.—P.m.r. spectrum of II in acetone-d_6 measured at 60 Mc./sec.$^{-1}$ (<5% w./v.).

tomer has increased at the expense of the tetrazolo tautomer when compared with the equilibrium involving I. Thus for a given solvent the equilibrium constant for II is larger than that for I (see Table I). This establishes that the greater stability of the tetrazole tautomer relative to the azido tautomer in I is a result of the inductive effect of the methyl groups.[8] The p.m.r. spectrum of I in methanol-d_4 shows that approximately 80% of the methyl protons exchange with the deuterium of the solvent on standing at room temperature for 24 hr. Isotopic substitution, however, has no observable effect on the value of K_T calculated from relative absorptions of the ring protons of Ia and Ib measured at zero time and 24 hr. later.

In the p.m.r. spectrum of II the absorption from each proton of IIa appears as a quartet (see Figure 3). Analysis of this part of the spectrum indicates that it is less adequately described as an AMX spectrum[15] than as an ABX spectrum.[16] The AB part is attributed to the signals from the 5- and 7-protons and the X part to the signals from the 6-proton. As expected the symmetrical azido tautomer (IIb) exhibits two signals, a triplet for the 5-proton and a doublet for the equivalent 4- and 6-protons (see Figure 3). Although a difference in the

(15) J. D. Roberts, "An Introduction to the Analysis of Spin–Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961.

(16) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

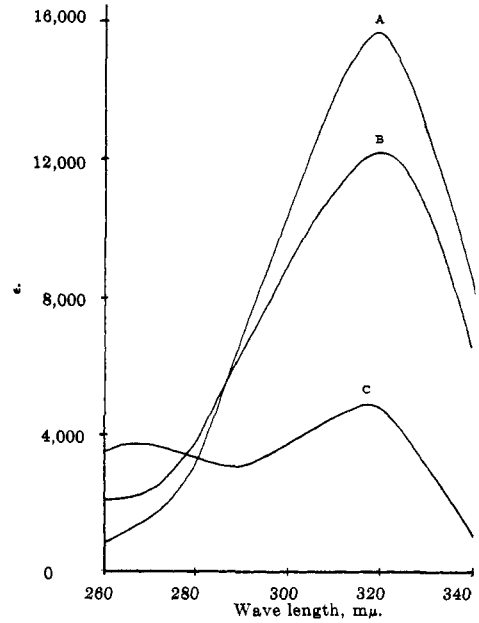


Figure 4.—Ultraviolet absorption spectra[18] (in 0.1 N sodium hydroxide) of IIIa (curve A); IIIc (curve B); initial spectrum of I (curve C).

polarity of IIa and IIb seems likely, the *a priori* prediction of the direction of a concentration effect on the equilibrium constant of II is difficult. Unexpectedly the constancy of K_T for 10 and 32% solutions of II in dimethyl sulfoxide-d_6 indicates the absence of such an effect for II under these conditions.

The second equilibrium, between I and IIIa, is pH dependent. A solution of I in 0.1N sodium hydroxide initially shows peaks at 265 and 319 mμ with the latter increasing at the expense of the former (see Figure 4, curve C). The 265-mμ peak disappears within 1 hr. (see Figure 4, curve A) and the sodium salt of IIIa can then be isolated. Acidification of a solution of the salt, however, regenerates the tetrazolo[1,5-*a*]pyrimidine. The structure of the salt was confirmed by elemental analyses, by its p.m.r. spectrum, and by a comparison of its ultraviolet spectrum with that of IIIc (see Figure 4, curve B). The synthesis of IIIc from 2-allyl-5-aminotetrazole (IV)[17] and acetylacetone is similar to the method used to prepare I, but the formation of a tetrazolo[1,5-*a*]pyrimidine is blocked by the allyl group. Thus, in contrast to IIIa, hydrolysis of IIIc to IV occurs in an acidic medium. Finally, the p.m.r. spectrum[19] of the salt of IIIa exhibits methyl signals (in p.p.m. on the τ-scale) at 8.01 (7-CH_3) and 7.73 (5-CH_3) (doublet) (J = 0.5 c.p.s.), and proton signals at 4.82 (6-H) (multiplet) and −2.60 (7-OH or tetrazole NH depending on the site of salt formation). That the salt exists in the enolate form, however, is consistent with the presence of one proton at C-6.

Experimental[4]

The Action of Sodium Hydroxide on I.—A solution of 5,7-dimethyltetrazolo[1,5-*a*]pyrimidine (Ia) (200 mg., 1.34 mmoles) in water (10 ml.) and tetrahydrofuran (2 ml.) containing 1 N sodium hydroxide (1.0 ml.) was stirred at room temperature overnight. This solution was evaporated to dryness, the residue

(17) R. A. Henry and W. C. Finnegan, *J. Am. Chem. Soc.*, **76**, 923 (1954).

(18) The peaks appeared to be unstable except for that of IIIa.

(19) See structure III in the reaction chart for the numbering system used.

was washed with tetrahydrofuran (20 ml.), and the hygroscopic product (IIIa) was dried *in vacuo* over phosphorus pentoxide at 78° for 18 hr.: yield, 170 mg.; *this solid decomposes rapidly* without melting above 200°; λ_{max} in mμ ($\epsilon \times 10^{-3}$) at pH 7, 320 (15.3), and at pH 13, 319 (15.7); $\bar{\nu}_{max}$ in cm.$^{-1}$ 3435 (broad, OH or NH), 2995, 2965, 2920, and 2860 (aliphatic CH), 1630, 1605, 1555, and 1540 (C=C, C=N).

Anal. Calcd. for $C_6H_3NaN_5O$: C, 38.10; H, 4.23; N, 37.05. Found: C, 37.91; H, 4.10; N, 37.17.

The Condensation of Acetylacetone with IV.—A solution of 2-allyl-5-aminotetrazole (IV, 1.0 g.) in toluene (25 ml.) containing acetylacetone (1.0 ml.) and piperidine (2 drops) was refluxed under a water separator for 21 hr. During the reflux period 20 ml. of the toluene escaped. Addition of petroleum ether (25 ml.) to the remaining liquid deposited 890 mg. of unreacted IV. The filtrate from IV was evaporated to a small volume, and the residue was distilled under high vacuum to give IIIc: yield, 100 mg.; λ_{max} in mμ at pH 7, 318, and at pH 13, 319; $\bar{\nu}_{max}$ in cm.$^{-1}$ (contact film) 3420, 3340, and 3220 (OH), 2990, 2940, and 2860 (aliphatic CH), and 1630, 1600, 1550, and 1540 (C=C, C=N).

Anal. Calcd. for $C_9H_{13}N_5O$: C, 52.20; H, 6.28; N, 33.80. Found: C, 51.84; H, 5.65; N, 33.77.

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Studies on the Azidoazomethine–Tetrazole Equilibrium. II. 4-Azidopyrimidines[1]

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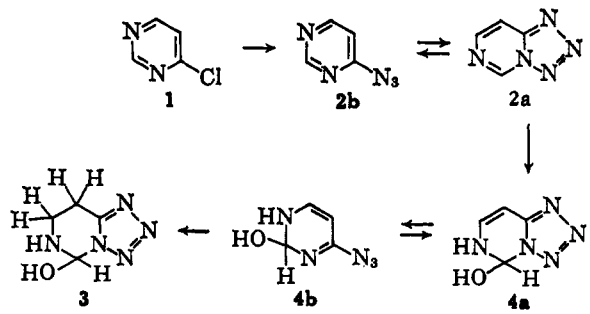
The preparation of a number of compounds for the study of the 4-azidopyrimidine–tetrazolo[1,5-*c*]pyrimidine equilibrium by means of infrared and proton magnetic resonance spectrometry is described; equilibrium constants were calculated from the ratio of the amount of the azido tautomer to that of the tetrazolo tautomer. The interaction of 4-chloropyrimidine hydrochloride (**1**) and sodium azide gave a mixture of 4-azidopyrimidine (**2b**) and tetrazolo[1,5-*c*]pyrimidine (**2a**) in which the latter is the major tautomer. This mixture readily combined with water to give a covalent hydrate, identified as 5,6-dihydro-5-hydroxytetrazolo[1,5-*c*]pyrimidine (**4a**). In the 5-amino-4-azido-6-chloropyrimidine–8-amino-7-chlorotetrazolo[1,5-*c*]pyrimidine system (**6**) the tetrazolo tautomer (**6a**) is the major form in the solid state, but only the azido form can be detected in a trifluoroacetic acid solution, a result of protonation. Also, conversion of the amino group of **6** to either an ethoxymethyleneamino or an acetamido group causes tetrazole destabilization to give mainly the azido tautomers. The presence of an acetyl or trifluoroacetyl group on the amino group of the 5-amino-4,6-diazidopyrimidine–8-amino-7-azidotetrazolo[1,5-*c*]pyrimidine system favors the (di)azido tautomers. The value of the equilibrium constant for the N-(4-amino-6-azido-5-pyrimidinyl)acetamide–8-acetamido-7-aminotetrazolo[1,5-*c*]pyrimidine system (**13**) in dimethyl sulfoxide-d_6 is larger than that of systems **11** and **12**, which suggests that the amino group of **13** is involved in hydrogen bonding.

Although the reaction of chloroazomethine heterocycles with sodium azide to give either azido derivatives or the tautomeric tetrazolo derivatives is well documented,[2] the investigation of the azidoazomethine–tetrazole equilibrium has only recently received attention.[3] In a previous paper we reported that **6** existed mainly as the 8-amino-7-chlorotetrazolo[1,5-*c*]pyrimidine (**6a**) and that **7** existed mainly as the 4-azido-6-chloro-5-ethoxymethyleneaminopyrimidine (**7b**).[3c] This observation prompted the synthesis of additional compounds of this system and a study of the effect of solvent and of certain electron-donating and electron-attracting groups on the 4-azidopyrimidine–tetrazolo-[1,5-*c*]pyrimidine equilibrium. As in a recent paper on the 2-azidopyrimidine–tetrazolo[1,5-*a*]pyrimidine equilibrium,[3f] the infrared and proton magnetic resonance spectra were used to detect and to determine the relative amounts of each tautomer in a given solvent.



Treatment of freshly sublimed 4-chloropyrimidine hydrochloride (**1**) with sodium azide in N,N-dimethylformamide at 85° gave a 23% yield of system **2**. In contrast to the isomeric 2-azidopyrimidine–tetrazolo-[1,5-*a*]pyrimidine system,[3f,4] **2** readily combined with water to give a covalent hydrate. When water was involved in the work-up, the hydrate was the only product isolated from the reaction of the hydrochloride of **1** with sodium azide in dimethyl sulfoxide at room temperature; it was assigned the structure **4a**, which would result from the addition of water to the 5,6 C=N bond of **2a**.[5] The structure of **4a** was indicated by (1) elemental analyses, (2) a molecular weight de-

(1) *This investigation was supported by funds from the C. F. Kettering* Foundation and the Cancer Chemotherapy National Service Center, National Cancer Institutes, National Institutes of Health, Contract No. PH-43-64-51.

(2) F. R. Benson, L. W. Hartzel, and E. A. Otten, *J. Am. Chem. Soc.*, **76**, 1858 (1954), and references therein.

(3) (a) J. H. Boyer and E. J. Miller, Jr., *ibid.*, **81**, 4671 (1959); (b) J. H. Boyer and H. W. Hyde, *J. Org. Chem.*, **25**, 458 (1960); (c) C. Temple, Jr., R. L. McKee, and J. A. Montgomery, *ibid.*, **27**, 1671 (1962). (d) Y. N. Sheinker, I. Ya. Postovskii, N. P. Bednyagina, L. B. Senyavina, and L. F. Lipatova, *Dokl. Akad. Nauk. SSSR*, **141**, 1388 (1961); (e) I. Ya. Postovskii and I. N. Goncharova, *Zh. Obshch. Khim.*, **33**, 2334 (1963); (f) C. Temple, Jr., and J. A. Montgomery, *J. Org. Chem.*, **30**, 826 (1965).

(4) K. Shirakawa, Japanese Patent 777 (Feb. 6, 1957); *Chem. Abstr.*, **52**, 4699*h* (1958).

(5) In addition a solid sample of **2** in a vial was converted to **4a**—apparently by the absorption of atmospheric moisture.