Synthesis of Imidazo[4,5-*e*]-*as*-triazine (6-Azapurine) DerivativesFUMIO YONEDA, MITSUKO NOGUCHI, MITSUE NODA,^{1a)}
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6-Benzylidenehydrazino-3-methyluracils were treated with sodium nitrite in acetic acid to give the corresponding 5-nitrosouracils. Dehydrative cyclization of the 5-nitrosouracils with acetic anhydride afforded 6-substituted 3-methyl-7-azalumazines, ethylation of which gave 6-substituted 1-ethyl-3-methyl-7-azalumazines.

Treatment of these 7-azalumazines thus obtained and 6-substituted 1,3-dimethyl-7-azalumazines with alcoholic sodium hydroxide caused a benzylic acid type rearrangement followed by decarboxylation and oxidation by air to give the respective 5*H*-imidazo[4,5-*e*]-*as*-triazine-6(7*H*)-ones (6-azapurines). Prolonged hydrolysis of 3-substituted 7-ethyl-5-methyl-5*H*-imidazo[4,5-*e*]-*as*-triazine-6(7*H*)-ones with alcoholic sodium hydroxide caused the ring cleavage to give 3-substituted 6-ethylamino-5-methylamino-*as*-triazines, which were fused with benzamidine hydrochloride to give rise to 3-substituted 7-ethyl-6-phenylimidazo[4,5-*e*]-*as*-triazines.

Keywords—6-azapurine; imidazo[4,5-*e*]-*as*-triazine; ring transformation; ring contraction; pyrimido[4,5-*e*]-*as*-triazine; 7-azalumazine (7-azapteridine); benzylic acid type rearrangement; 6-ethylamino-5-methylamino-*as*-triazine

A number of 8-azapurine (*s*-triazolo[4,5-*d*]pyrimidine) derivatives²⁾ have been synthesized as potential purine antagonists since discovery of antitumor activity in 8-azapurines.³⁾ Also, 2-azapurine (imidazo[4,5-*d*]-*v*-triazine) derivatives⁴⁾ have been prepared and found to be highly cytotoxic, although they were not effective as anticancer agents.⁵⁾ Though the isomeric 6-azapurine (imidazo[4,5-*e*]-*as*-triazine) ring system is of interest from a chemical as well as from a potential biological point of view, any report concerning this type of substances has not been found until two laboratories reported recently two independent synthetic routes.^{6,7)} Kaji and coworker⁷⁾ have described the synthesis of 6-azapurines consisting of the cyclization of 5,6-diamino-*as*-triazine-3(2*H*)-ones with one-carbon reagents. We now present the detailed account of a new approach to 6-azapurine (imidazo[4,5-*e*]-*as*-triazine) derivatives which involves a benzylic acid type rearrangement of 7-azalumazine (pyrimido[4,5-*e*]-*as*-triazine) derivatives.^{6b)}

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- 2) a) R.K. Robins, "Heterocyclic Compounds," Vol. 8, ed. R.C. Elderfield, John Wiley, and Sons, 1967, p. 162, and references cited therein; b) A. Albert, *J. Chem. Soc. (B)*, 1966, 427; c) J.W. Bunting and D.D. Perrin, *ibid.*, 1966, 433; d) A. Albert and K. Tratt, *J. Chem. Soc. (C)*, 1968, 344; e) A. Albert, *ibid.*, 1968, 2076; f) A. Albert, *ibid.*, 1969, 152; g) H.U. Blank, I. Wempen, and J.J. Fox, *J. Org. Chem.*, 35, 1131 (1970); h) Y. Maki, M. Suzuki, K. Izuta, and S. Iwai, *Chem. Pharm. Bull. (Tokyo)*, 22, 1269 (1974); i) K. Senga, Y. Kanamori, S. Nishigaki, and F. Yoneda, *ibid.*, 24, 1917 (1976); j) K. Senga, M. Ichiba, and S. Nishigaki, *Heterocycles*, 6, 1915 (1977).
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Syntheses of 7-Azalumazine (Pyrimido[4,5-*e*]-*as*-triazine) Precursors

It is known that the treatment of 6-benzylidenehydrazino-3-methyluracil in acetic acid with saturated aqueous sodium nitrite gives 6-benzylidenehydrazino-3-methyl-5-nitrosouracil (Ia).⁸⁾ By this method, 5-nitrosouracil derivatives (Ib—g) were obtained from the corresponding 6-benzylidenehydrazino-3-methyluracils⁹⁾ (Table I).

TABLE I. 6-Benzylidenehydrazino-3-methyl-5-nitrosouracils

Compd. No.	R	mp (°C)	Yield (%)	Formula	Analysis (%)					
					Calcd.			Found		
					C	H	N	C	H	N
Ia	C ₆ H ₅	206	92	C ₁₂ H ₁₁ N ₅ O ₃	52.74	4.06	25.63	52.68	4.12	25.47
Ib	4-Cl-C ₆ H ₄	224	89	C ₁₂ H ₁₀ ClN ₅ O ₃	46.84	3.28	22.76	46.93	3.28	22.46
Ic	3,4-Cl ₂ -C ₆ H ₃	230	83	C ₁₂ H ₉ Cl ₂ N ₅ O ₃	42.12	2.65	20.47	42.25	2.55	20.51
Id	4-CH ₃ O-C ₆ H ₄	245	75	C ₁₃ H ₁₃ N ₅ O ₄	51.48	4.32	23.09	51.55	4.30	23.34
Ie	3,4-CH ₂ O ₂ -C ₆ H ₃	233	75	C ₁₃ H ₁₁ N ₅ O ₅	49.21	3.49	22.08	49.07	3.46	21.79
If	4-(CH ₃) ₂ N-C ₆ H ₄	220	70	C ₁₄ H ₁₆ N ₆ O ₃	53.16	5.10	26.57	53.22	5.19	26.48
Ig	4-CH ₃ -C ₆ H ₄	236	81	C ₁₃ H ₁₃ N ₅ O ₃	54.35	4.56	24.38	54.33	4.55	24.30

Refluxing of these 5-nitrosouracil derivatives (Ia—g) in acetic anhydride for 1 hr caused dehydrative cyclization to give the respective 6-substituted 3-methyl-7-azalumazines (3-substituted 6-methylpyrimido[4,5-*e*]-*as*-triazine-5,7(6*H*,8*H*)-diones) (IIa—g) in 40—70% yields,

8) F. Yoneda and T. Nagamatsu, *Chem. Pharm. Bull.* (Tokyo), **23**, 1885 (1975).

9) F. Yoneda and T. Nagamatsu, *Bull. Chem. Soc. Jpn.*, **48**, 1484 (1975).

which were in all respects identical with authentic samples¹⁰⁾ prepared by the demethylation of the corresponding toxoflavin derivatives (Table II).

TABLE II. 6-Substituted 3-Methyl-7-azalumazines (3-Substituted 6-Methylpyrimido[4,5-*e*]-*as*-triazine-5,7(6*H*,8*H*)-diones)

Compd. No.	R	mp (°C)	Yield (%)	Formula	Analysis (%)					
					Calcd.			Found		
					C	H	N	C	H	N
IIa	C ₆ H ₅	>320	46	C ₁₂ H ₉ N ₅ O ₂	56.47	3.55	27.44	56.23	3.62	27.31
IIb	4-Cl-C ₆ H ₄	>320	42	C ₁₂ H ₈ ClN ₅ O ₂	49.75	2.78	24.18	49.69	2.77	24.04
IIc	3,4-Cl ₂ -C ₆ H ₃	>320	68	C ₁₂ H ₇ Cl ₂ N ₅ O ₂	44.46	2.18	21.61	44.38	2.19	21.40
IId	4-CH ₃ O-C ₆ H ₄	>320	40	C ₁₃ H ₁₁ N ₅ O ₃	54.73	3.89	24.55	54.49	3.73	24.24
IIf	3,4-CH ₂ O ₂ -C ₆ H ₃	>320	47	C ₁₃ H ₉ N ₅ O ₄	52.18	3.03	23.41	52.22	3.25	23.23
IIg	4-(CH ₃) ₂ N-C ₆ H ₄	>320	42	C ₁₄ H ₁₄ N ₆ O ₂	56.37	4.73	28.18	56.22	4.65	28.23
IIg	4-CH ₃ -C ₆ H ₄	>320	58	C ₁₃ H ₁₁ N ₅ O ₂	57.99	4.09	26.02	58.13	4.00	26.10

6-Substituted 1,3-dimethyl-7-azalumazines (3-substituted 6,8-dimethylpyrimido[4,5-*e*]-*as*-triazine-5,7(6*H*,8*H*)-diones) (IIh—m) were obtained by the condensation of 6-amino-1,3-dimethyl-5-nitrosouracil with aldehyde hydrazones according to the procedure described previously.¹¹⁾

6-Substituted 1-ethyl-3-methyl-7-azalumazines (3-substituted 8-ethyl-6-methylpyrimido[4,5-*e*]-*as*-triazine-5,7(6*H*,8*H*)-diones) (II n—r) were obtained by ethylation of the corresponding 3-methyl-7-azalumazines (IIa—e) with ethyl iodide (Table III).

TABLE III. 6-Substituted 1-Ethyl-3-methyl-7-azalumazines (3-Substituted 8-Ethyl-6-methylpyrimido[4,5-*e*]-*as*-triazine-5,7(6*H*, 8*H*)-diones)

Compd. No.	R	mp (°C)	Yield (%)	Formula	Analysis (%)					
					Calcd.			Found		
					C	H	N	C	H	N
II n	C ₆ H ₅	234	98	C ₁₄ H ₁₃ N ₅ O ₂	59.35	4.63	24.72	59.28	4.64	24.39
II o	4-Cl-C ₆ H ₄	246	95	C ₁₄ H ₁₂ ClN ₅ O ₂	52.92	3.81	22.04	53.01	3.80	21.85
II p	3,4-Cl ₂ -C ₆ H ₃	258	96	C ₁₄ H ₁₁ Cl ₂ N ₅ O ₂	47.74	3.15	19.89	47.83	3.16	19.63
II q	4-CH ₃ O-C ₆ H ₄	225	95	C ₁₅ H ₁₅ N ₅ O ₃	57.50	4.83	22.34	57.83	4.83	21.98
II r	3,4-CH ₂ O ₂ -C ₆ H ₃	230	94	C ₁₅ H ₁₃ N ₅ O ₄	55.04	4.00	21.40	54.87	4.02	21.18

10) a) F. Yoneda and T. Nagamatsu, *Tetrahedron Lett.*, 1973, 1577; b) F. Yoneda and T. Nagamatsu, *Chem. Pharm. Bull.* (Tokyo), 23, 2001 (1975).

11) a) F. Yoneda, M. Kanahori, K. Ogiwara, and S. Nishigaki, *J. Heterocycl. Chem.*, 7, 1443 (1970); b) F. Yoneda and T. Nagamatsu, *Bull. Chem. Soc. Jpn.*, 48, 2884 (1975).

Transformation of 7-Azalumazines into 6-Azapurines (Imidazo[4,5-*e*]-*as*-triazines)

Treatment of the 7-azalumazine derivatives (IIa—r) thus obtained with 10% alcoholic sodium hydroxide under the conditions indicated in Table IV, followed by acidification (evolution of carbon dioxide was observed here) with acetic acid, resulted in the formation of the respective 3-substituted 5-methyl- (IIIa—g), 3-substituted 5,7-dimethyl- (IIIh—m) and 3-substituted 7-ethyl-5-methyl-5*H*-imidazo[4,5-*e*]-*as*-triazine-6(7*H*)-ones (III_n—r) (Table IV).

TABLE IV. Transformation of 7-Azalumazines into 6-Azapurines

Starting material	Reaction conditions	No.	6-Azapurine		mp (°C)	Yield (%)	Formula	Analysis (%)		
			R ¹	R ²				Calcd. (Found)		
								C	H	N
IIa	Reflux 1 hr	IIIa	H	C ₆ H ₅	283	61	C ₁₁ H ₉ N ₅ O	58.14 (58.20)	3.99 4.01	30.82 30.64
IIb	Reflux 1 hr	IIIb	H	4-Cl-C ₆ H ₄	266	52	C ₁₁ H ₈ ClN ₅ O	50.49 (50.44)	3.08 3.09	26.77 26.80
IIc	Reflux 1 hr	IIIc	H	3,4-Cl ₂ -C ₆ H ₃	284	49	C ₁₁ H ₇ Cl ₂ N ₅ O	44.61 (44.70)	2.38 2.40	23.65 23.51
IId	Reflux 1 hr	IIId	H	4-CH ₃ O-C ₆ H ₄	292	42	C ₁₂ H ₁₁ N ₅ O ₂	56.02 (55.88)	4.31 4.51	27.23 27.21
IIf	Reflux 2 hr	IIIe	H	3,4-CH ₂ O ₂ -C ₆ H ₃	324	40	C ₁₂ H ₉ N ₅ O ₃	53.14 (52.98)	3.34 3.33	25.82 25.79
IIg	Reflux 2 hr	IIIg	H	4-(CH ₃) ₂ N-C ₆ H ₄	281	51	C ₁₃ H ₁₄ N ₆ O	57.76 (58.02)	5.22 5.25	31.10 30.09
IIh	Reflux 1 hr	IIIh	H	4-CH ₃ -C ₆ H ₄	296	53	C ₁₂ H ₁₁ N ₅ O	59.74 (59.68)	4.60 4.45	29.03 28.83
IIi	60° 10 min	IIIi	CH ₃	C ₆ H ₅	203	71	C ₁₂ H ₁₁ N ₅ O	59.74 (59.88)	4.60 4.35	29.03 28.90
IIj	60° 10 min	IIIj	CH ₃	4-Cl-C ₆ H ₄	251	65	C ₁₂ H ₁₀ ClN ₅ O	52.27 (52.30)	3.66 3.62	25.40 25.28
IIk	60° 30 min	IIIk	CH ₃	3,4-Cl ₂ -C ₆ H ₃	247	55	C ₁₂ H ₉ Cl ₂ N ₅ O	46.47 (46.59)	2.93 2.88	22.58 22.42
IIl	60° 30 min	IIIl	CH ₃	4-CH ₃ O-C ₆ H ₄	255	58	C ₁₃ H ₁₃ N ₅ O ₂	57.56 (57.60)	4.83 4.81	25.82 25.62
IIm	60° 30 min	III _m	CH ₃	3,4-CH ₂ O ₂ -C ₆ H ₃	330	51	C ₁₃ H ₁₁ N ₅ O ₃	54.73 (54.75)	3.89 3.85	24.55 24.20
II _n	60° 30 min	III _n	CH ₃	4-(CH ₃) ₂ N-C ₆ H ₄	290	87	C ₁₄ H ₁₆ N ₆ O	59.14 (59.30)	5.67 5.55	29.56 29.61
II _o	Reflux 1 hr	III _o	C ₂ H ₅	C ₆ H ₅	190	70	C ₁₃ H ₁₃ N ₅ O	61.16 (60.95)	5.13 5.02	27.44 27.23
II _p	Reflux 1 hr	II _p	C ₂ H ₅	4-Cl-C ₆ H ₄	225	68	C ₁₃ H ₁₂ ClN ₅ O	53.89 (54.02)	4.18 4.17	24.17 23.79
II _q	Reflux 1 hr	III _q	C ₂ H ₅	3,4-Cl ₂ -C ₆ H ₃	206	58	C ₁₃ H ₁₁ Cl ₂ N ₅ O	48.16 (48.21)	3.42 3.45	21.61 21.53
II _r	Reflux 1 hr	III _r	C ₂ H ₅	4-CH ₃ O-C ₆ H ₄	243	84	C ₁₄ H ₁₅ N ₅ O ₂	58.93 (59.04)	5.30 5.28	24.55 24.36
II _r	Reflux 1 hr	III _r	C ₂ H ₅	3,4-CH ₂ O ₂ -C ₆ H ₃	218	72	C ₁₄ H ₁₃ N ₅ O ₃	56.18 (56.21)	4.38 4.38	23.40 23.29

The assigned structures of compounds III were deduced on the basis of elemental analyses, molecular weights as determined by mass spectrometry, IR (the presence of a carbonyl band at 1760 cm⁻¹ region) and NMR data, and by consideration of their probable mode of forma-

tion (Chart 3). Furthermore, compounds IIIa–f were converted into the 5,7-dimethyl derivatives (IIIh–m) by methylation with methyl iodide and potassium carbonate in dimethylformamide for identification purpose.

We suggest that these 6-azapurines are formed from 7-azalumazines by a benzilic acid type rearrangement, followed by decarboxylation and oxidation by air, as depicted in Chart 3. An analogous ring contraction was reported in the reaction of 1,3,7,9-tetramethylpy-

TABLE V. 3-Substituted 6-Ethylamino-5-methylamino-*as*-triazines

Compd. No.	R	mp (°C)	Yield (%)	Formula	Analysis (%)					
					Calcd.			Found		
					C	H	N	C	H	N
IVa	C ₆ H ₅	201	63	C ₁₂ H ₁₅ N ₅	62.86	6.60	30.55	62.90	6.58	30.29
IVb	4-Cl-C ₆ H ₄	220	56	C ₁₂ H ₁₄ ClN ₅	54.65	5.35	26.56	54.62	5.29	26.19
IVc	3,4-Cl ₂ -C ₆ H ₃	213	60	C ₁₂ H ₁₃ Cl ₂ N ₅	48.33	4.39	23.49	48.41	4.35	23.38
IVd	4-CH ₃ O-C ₆ H ₄	199	46	C ₁₃ H ₇ N ₅ O	60.21	6.61	27.01	59.99	6.60	26.73
IVe	3,4-CH ₂ O ₂ -C ₆ H ₃	223	85	C ₁₈ H ₁₅ N ₅ O ₂	57.13	5.53	25.63	57.21	5.54	25.55

rimido[5,4-*g*]pteridine-2,4,6,8(1*H*,3*H*,7*H*,9*H*)-tetrone 5-oxide with sodium hydroxide giving 1,3-dimethyl-5-methylaminocarbonyl-6-methylamino-1*H*-imidazo[4,5-*b*]pyrazin-2(3*H*)-one.¹²⁾

When prolonged hydrolysis of compounds III*n*—r with 10% alcoholic sodium hydroxide was carried out, the corresponding ring-opened products, 6-ethylamino-5-methylamino-*as*-triazine derivatives (IVa—e) were obtained (Table V). The structures of IVa—e were ascertained by elemental analyses, molecular weight determination by mass spectrometry and by spectral data (the presence of two NH absorptions at 3270 and 3170 cm⁻¹ regions and disappearance of a carbonyl band at 1760 cm⁻¹ region).

Fusion of IVa and IVb with excess benzamidine hydrochloride at 180° caused the elimination of methylamine and ammonia and gave rise to 3-substituted 7-ethyl-6-phenylimidazo[4,5-*e*]-*as*-triazines (2-substituted 7-ethyl-8-phenyl-6-azapurines) (Va and Vb). The elemental analyses and spectral data of Va and Vb (disappearance of two NH absorptions of IV in IR and survival of ethyl signals in NMR) were consistent with the assigned structures.

Table VI gives ultraviolet absorption data for some 6-azapurines, in which the expected hypochromic shifts were observed as compared with absorptions of the corresponding 7-azaluminazines.¹³⁾

TABLE VI. UV Maxima of 6-Azapurines

Compd. No.	$\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ)
IIIa	306(3.68), 287 sh(3.69), 271 sh(3.74), 243(3.97)
IIIb	308(3.78), 289 sh(3.83), 278(3.84), 247(4.02)
IIIc	320 sh(3.86), 279(4.25), 253(4.19)
IIId	310 sh(3.60), 241(4.11)
IIIe	310(3.98), 271(4.08), 245(4.32)
IIIf	309(4.07), 275(4.25), 249(4.39)
IIIg	309(3.81), 270(3.88), 245(4.15)
IIIh	309(4.11), 289(4.25), 249(4.36)
Va	337(3.66), 270 sh(3.78), 259(3.87)
Vb	338(3.99), 289 sh(4.00), 264.5(4.26)
IIh ^{a)}	375(3.55), 278(4.45)

a) 1,3-Dimethyl-6-phenyl-7-azaluminazine.¹³⁾

Experimental¹⁴⁾

6-Benzylidenehydrazino-3-methyl-5-nitrosouracils (Ia—g). **General Procedure**—To a stirred suspension of a 6-benzylidenehydrazino-3-methyluracil (0.01 mol) in AcOH (50 ml) was added saturated aqueous solution of NaNO₂ (0.015 mol) drop by drop under cooling at 5°. The reaction solution was then stirred at room temperature for 2 hr, during which time crystals were separated. The crystals were collected by filtration, washed with H₂O, and recrystallized from EtOH or DMF to give pale green microcrystalline powder of 5-nitrosouracil derivatives (Ia—g) (Table I).

6-Substituted 3-Methyl-7-azaluminazines (3-Substituted 6-Methylpyrimido[4,5-*e*]-*as*-triazine-5,7(6*H*,8*H*)-diones) (IIa—g). **General Procedure**—The 5-nitrosouracil derivatives (Ia—g) (0.01 mol) thus obtained were refluxed in acetic anhydride (30 ml) for 3 hr. The reaction solution was evaporated into dryness under reduced pressure and the residue was treated with EtOH to cause the separation of yellow crystals which were filtered off and dried. Recrystallization from DMF—EtOH (1:1) gave yellow microcrystalline powder of the corresponding 7-azaluminazines which were identical with authentic samples.¹⁰⁾

6-Substituted 1-Ethyl-3-methyl-7-azaluminazines (3-Substituted 8-Ethyl-6-methylpyrimido[4,5-*e*]-*as*-triazine-5,7(6*H*,8*H*)-diones) (II*n*—r). **General Procedure**—A mixture of a 6-substituted 3-methyl-7-

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13) F. Yoneda, T. Nagamatsu, and K. Shinomura, *J. Chem. Soc. Perkin I*, **1976**, 713.

14) All melting points were uncorrected. NMR spectra were determined with a JEOL-PMX 60 spectrometer (tetramethylsilane as internal standard). Identity of compounds was confirmed by comparison of infrared spectra (Nujol mulls) with JASCO IR-1A spectrophotometer.

azalumazine (IIa—e) (0.1 mol), ethyl iodide (18.7 g, 0.12 mol) and K_2CO_3 (27.6 g, 0.2 mol) in DMF (150 ml) were refluxed for 2 hr. After cooling, the reaction mixture was diluted with H_2O (150 ml) to cause the separation of pale yellow crystals, which were filtered off, washed with H_2O and dried. Recrystallization from EtOH gave pale yellow needles (Table III).

Transformation of 7-Azalumazines (II) into 6-Azapurines (III). **General Procedure**—To 10% ethanolic sodium hydroxide (20 ml) was added a 7-azalumazine (0.004 mol) and the mixture was refluxed under the conditions indicated in Table IV. After cooling, the reaction mixture was acidified with AcOH and evaporated *in vacuo* into dryness. The residue was treated with H_2O and the separated crystals were filtered off and recrystallized from EtOH or DMF to give colorless needles of the respective 6-azapurines (Table IV).

3-Substituted 6-Ethylamino-5-methylamino-*as*-triazines (IVa—e). **General Procedure**—To 10% ethanolic sodium hydroxide (20 ml) was added a 7-ethyl-5-methyl-5*H*-imidazo[4,5-*e*]-*as*-triazine-6(7*H*)-one (III*n*—r) (0.004 mol) and the mixture was refluxed for 6 hr. After cooling, the reaction mixture was neutralized with AcOH to cause the separation of colorless crystals, which were collected by filtration, washed with H_2O and recrystallized from EtOH to give colorless microcrystalline powder of a 6-ethylamino-5-methylamino-*as*-triazine (IVa—e) (Table V).

3,6-Diphenyl-7-ethylimidazo[4,5-*e*]-*as*-triazine (2,8-Diphenyl-7-ethyl-6-azapurine) (Va)—A mixture of 6-ethylamino-5-methylamino-3-phenyl-*as*-triazine (IVa) (0.3 g, 0.0013 mol) and benzamidine hydrochloride (0.6 g, 0.0038 mol) was fused at 180° for 1 hr. After cooling, the reaction mixture was triturated in H_2O and the crystals were filtered off and dried. Recrystallization from DMF–EtOH (1:1) gave colorless needles (0.3 g, 79%), mp 195°. *Anal.* Calcd. for $C_{18}H_{15}N_5$: C, 71.74; H, 5.02; N, 23.24. Found: C, 71.86; H, 5.11; N, 23.01.

3-(4-Chlorophenyl)-7-ethyl-6-phenylimidazo[4,5-*e*]-*as*-triazine [2-(4-Chlorophenyl)-7-ethyl-8-phenyl-6-azapurine] (Vb)—A mixture of 3-(4-chlorophenyl)-6-ethylamino-5-methylamino-*as*-triazine (IVb) (0.3 g, 0.001 mol) and benzamidine hydrochloride (0.6 g, 0.0038 mol) was treated as above to give colorless crystals (0.31 g, 81%), mp 198°. *Anal.* Calcd. for $C_{18}H_{14}ClN_5$: C, 64.38; H, 4.20; N, 20.86. Found: C, 64.39; H, 4.23; N, 20.48.

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