2,6-Dimethyl-4,5-diamino-3(2*H*)pyridazinone (XXV)——XXIIIb (2.3 g) was fused at 220—230° for 30 minutes, resultant black solid was recrystallized from MeOH (charcoal) to give 1.22 g (53%) of yellow prisms, mp>300°. *Anal.* Calcd. for $C_6H_{10}ON_4$: C, 46.74; H, 6.54; N, 36.34. Found: C, 46.70; H, 6.63; N, 36.05.

Acknowledgement We are indebted to Mrs. H. Mazume for the elementary analysis and to Mr. N. Yamaguchi for the mesurement of infrared and ultraviolet spectra.

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Studies on the Synthesis of Pyridazine Derivatives. XIII.[1] Synthesis of Imidazo-[4,5-*d*]- and *v*-Triazolo[4,5-*d*]pyridazine Derivatives and Reaction of 4-Alkoxy-*v*-triazolo[4,5-*d*]pyridazines with Various Amines[2]

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Two methods have been reported about the syntheses of imidazo[4,5-*d*][4,5] and *v*-triazolo[4,5-*d*]pyridazines.[5,6] In the previous paper,[1] several new 4,5-diaminopyridazines were reported, in this paper will be described the cyclization of 4,5-diamino–compounds to imidazo[4,5-*d*]- and *v*-triazolo[4,5-*d*]pyridazines, and reaction of 4-alkoxy-*v*-triazolo[4,5-*d*]-pyridazines with various amines.

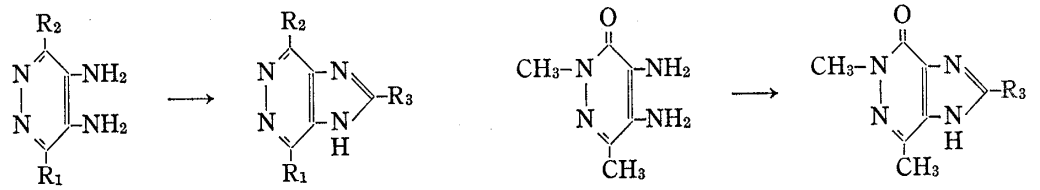
Imidazo[4,5-*d*]pyridazines

4,5-Diaminopyridazines (I) were cyclized to imidazo[4,5-*d*]pyridazines (II) in good yield by reaction with formic acid, formamide or ethyl orthoformate–acetic anhydrie. These results were summarized in Table I.

Imidazo[4,5-*d*]pyridazine (IIa) was prepared by treatment of 4,5-diaminopyridazine (Ia) with formic acid, on the other hand 4,5-diacetamidopyridazine (IV) was obtained by ethyl orthoformate and acetic anhydride method. Treatment of 3-methoxy-4,5-diaminopyridazine (Ib) with ethyl orthoformate and acetic anhydride gave 4-methoxyimidazo[4,5-*d*]pyridazine (IIb) in low yield accompanied with dealkylated product (IId). 4-Hydroxyimidazo[4,5-*d*]-pyridazine (IId) was prepared by follwing four methods i) reaction of 4,5-diamino-3(2*H*)-pyridazinone (Id) with ethyl orthofomate, ii) dechlorination of 4-hydroxy-7-chloroimidazo-[4,5-*d*]pyridazine (IIj) over palladium on charcoal, iii) reaction of 3-ethoxy-4,5-diaminopyridazine (Ic) with formamide, iv) treatment of 7-methylthiomidazo[4,5-*d*]pyridazine (IIe) with 28%

1) Part XII: M. Yanai, T. Kinoshita, S. Takeda, H. Sudaki and H. Watanabe, *Chem. Pharm. Bull.* (Tokyo), **18**, 1680 (1970).
2) A part of this paper was present at Kyushu Branch Meeting of Pharmaceutical Society of Japan, Kumamoto, Dec. 8, 1962 and Nagasaki, Sept. 28, 1968.
3) Location: *1–14 Bunkyo–machi, Nagasaki, 852, Japan.*
4) R.G. Jones, *J. Am. Chem. Soc.*, **78**, 159 (1956); T.S. Gardner, F.A. Smith, E. Wenis and J. Lee, *J. Org. Chem.*, **21**, 530 (1956); R.N. Castle and W.S. Seese, *ibid.*, **23**, 1534 (1958); M. Malm and R.N. Castle, *J. Heterocyclic Chem.*, **1**, 182 (1964).
5) T. Itai and S. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **8**, 999 (1960).
6) L. Erichomovitch and F.L. Chubb, *Can. J. Chem.*, **44**, 2095 (1966).

Table I.



I II or III , VIII IX

No.	Start. materials R_1	Start. materials R_2	Reaction Method[a]	Reaction Temp.	Reaction Time (hr)	No.	Products R_1	Products R_2	Products R_3	mp (°C)	Yield (%)	Appearance,[b] recryst. solv.	
Ia	H	H	A	reflux	12	IIa	H	H	H	308—309[c]	78	C.N.	MeOH
Ib	CH_3O	H	B	reflux	1	IIb	CH_3O	H	H	283—285	18	C.N.	MeOH
Ic	C_2H_5O	H	C	reflux	1/4	IId[d]	HO	H	H	>340	60	C.N.	water
Id	HO	H	B	reflux	3.5	IId	HO	H	H	>340	80	C.N.	water
Ie	CH_3S	H	B	reflux	6	IIe[d]	CH_3S	H	H	229—231	80	PYB.P.	MeOH
If	HS	H	A	reflux	6	IIf[d]	HS	H	H	310	48	PY.N.	water
Ig	CH_3O	CH_3	B	reflux	1	IIg	CH_3O	CH_3	H	[e]	60	C.N.	MeOH
Ih	C_2H_5O	CH_3	B	reflux	1	IIh	C_2H_5O	CH_3	H	>360	68	C.N.	MeOH
Ig	CH_3O	CH_3	C	reflux	2/3	IIi	HO	CH_3	H	>360	80	C.N.	MeOH
Ih	C_2H_5O	CH_3	C	reflux	2/3	IIi	HO	CH_3	H	>360	81	C.N.	MeOH
Ij	HO	Cl	A	reflux	4	IIj	HO	Cl	H	>350	75	C.P.	water
VIII	—	—	B	reflux	1/3	IXa	—	—	H	>300	59	C.N.	MeOH-water
Ig	CH_3O	CH_3	D	reflux	5	IIIg	CH_3O	CH_3	HS	245—300[f]	50	C.N.	MeOH
Ih	C_2H_5O	CH_3	D	reflux	5	IIIh	C_2H_5O	CH_3	HS	268—272	47	C.N.	MeOH
In	C_2H_5O	C_2H_5O	D	reflux	3	IIIn	C_2H_5O	C_2H_5O	HS	241—244	57	C.N.	water
VIII	—	—	D	reflux	3	IXb	—	—	HS	>300	22.5	O.C.	water

a) A: formic acid, B: ethyl orthoformate and acetic anhydride, C: formamide
b) C: colorless, PYB: pale yellowish brown, PY: pale yellow, O: orange, N: needles, P: prisms, C:crystals
c) decomp.
d) S.F. Martin and R.N. Castle, *J. Heterocyclic Chem.*, **6**, 93 (1969)
e) No definite melting point was observed, however a shrinking occured at about 220°.
f) No definite melting point was observed, however a shrinking occured at about 250°.

ammonium hydroxide, usually dealkylation was observed in the third method. 3-Methoxy-(ethoxy)-6-methyl-4,5-diaminopyridazine(Ig, Ih) reacted with carbon disulfide and sodium hydroxide in pyridine solution gave 2-mercapto-4-methoxy(ethoxy)-7-methylimidazo[4,5-*d*]-pyridazine (IIIg, IIIh) respectively. Treatment of compounds Ig and Ih with formamide gave same compound IIi (4-hydroxy-7-methylimidazo[4,5-*d*]pyridazine) in good yield. Treatment of 3-mercapto-4,5-diaminopyridazine (If) with formic acid gave 4-mercaptoimidazo-[4,5-*d*]pyridazine (IIf) which was obtained thiation of IId with phosphorous pentasulfide in dry pyridine.

Treatment of Ii with acetic anhydride gave 4,5-diacetamido-3-hydroxy-6-methylpyridazine (VI) and 2,7-dimethyl-4-hydroxyimidazo[4,5-*d*]pyridazine (VII), compound VI was converted to VII by fusion at 260°.

In case of cyclization of Id, Ij and If, there are two possible direction either imidazo-[4,5-*d*]pyridazines or oxazolo[5,4-*c*], thiazolo[5,4-*c*]pyridazine, the structure of all cyclization products of those diamino–compounds were determined in connection with compound IIe.

v-Triazolo[4,5-*d*]pyridazines

The cyclization of 4,5-diaminopyridazines to *v*-triazolo[4,5-*d*]pyridazines were treated with sodium nitrite in diluted acetic acid solution in 60—90% yield. Results were summarized in Table II.

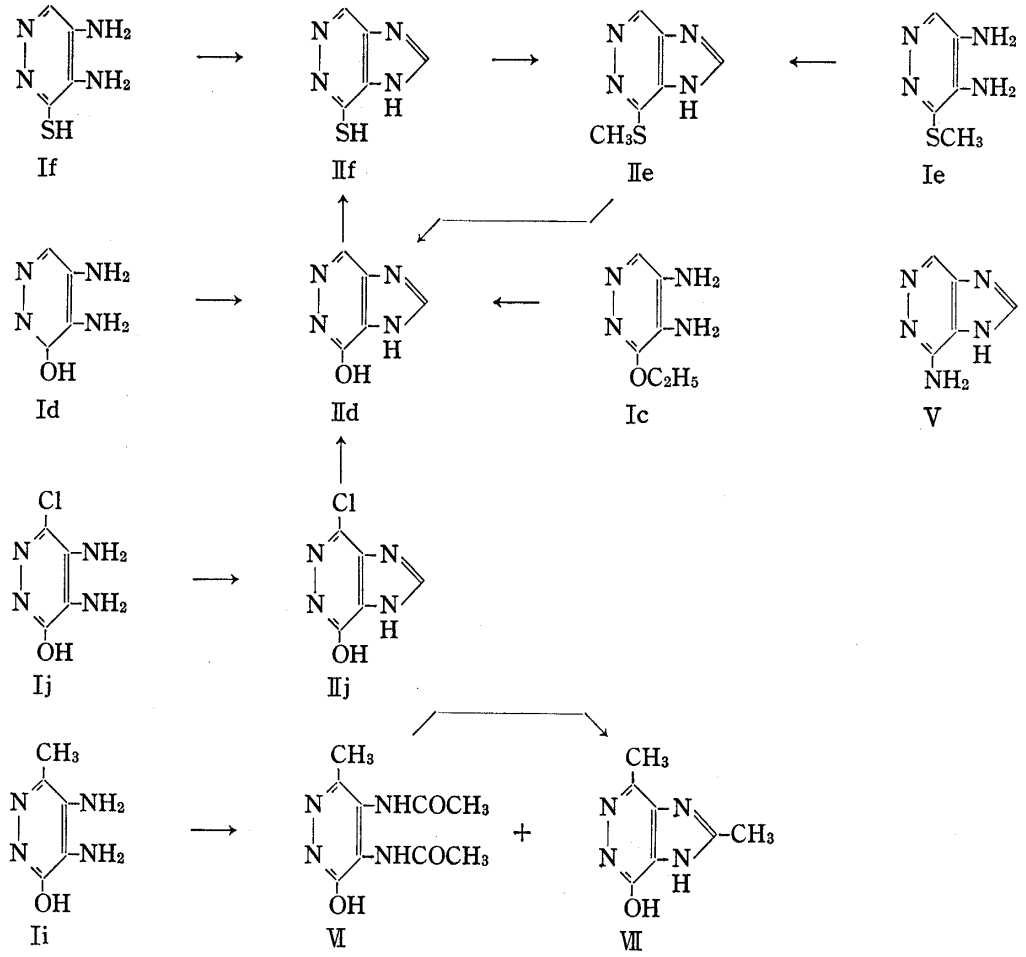
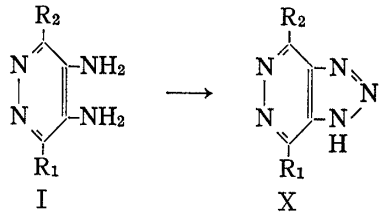


Chart 1

Table II.



Starting materials	Reaction temp. (°C)	Reaction time (min)	No.	Products R_1	Products R_2	mp (°C)	Yield (%)	Appearance[a]	Recryst. solv.
Ia	70—80	20	Xa	H	H	>300	63	PY.P.	water
Ib	70—80	20	Xb	CH_3O	H	141—142	47	C.P.	MeOH–water
			Xd[b]	HO	H	305—307[c]	6	PY.P.	water
Id	90—95	30	Xd[b]				66		
Ie	55	5	Xe[b]	CH_3S	H	224—225[c]	80	PY.P.	MeOH
If	90	30	Xf[b]	HS	H	>310	45	PY.P.	water
Ig	90—95	15	Xg	CH_3O	CH_3	156—157	70	C.N.	MeOH–water
Ih	90—95	15	Xh	C_2H_5O	CH_3	172—173	65	C.P.	MeOH–water
Ii	90—95	60	Xi	HO	CH_3	285—285.5[c]	79	C.S.	water
Ij	90	30	Xj	HO	Cl	229—230	70	PY.P.	water
Ik	55	40	Xk	NH_2	Cl	>320	80	N.	water
In	70—80	30	Xn	C_2H_5O	C_2H_5O	155—156	90	C.S.	EtOH
Ip			Xp	C_2H_5O	HO	239—241	70	C.P.	water

a) PY: pale yellow, C: colorless, P: prisms, N: needles, S: scales
b) S.F. Martin and R.N. Castle, *J. Heterocyclic Chem.*, **6**, 93 (1969)
c) decomp.

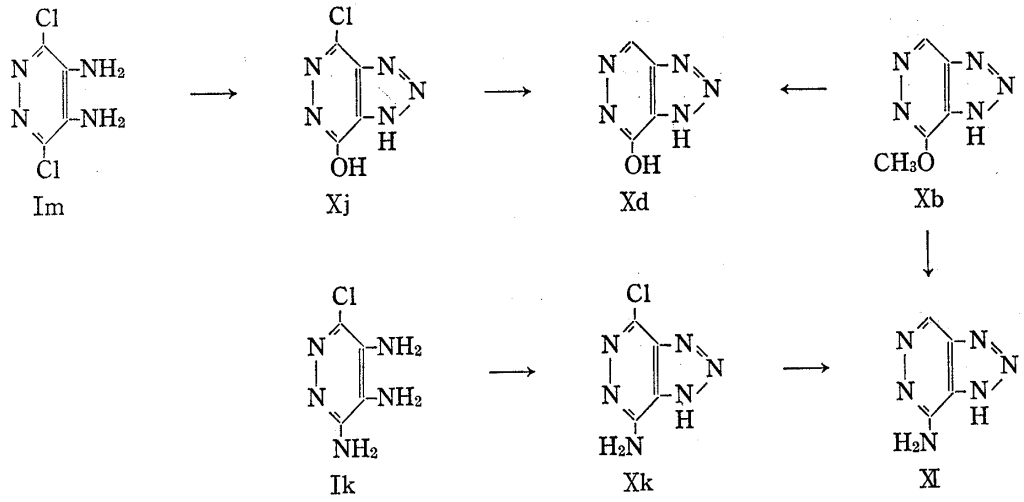


Chart 2

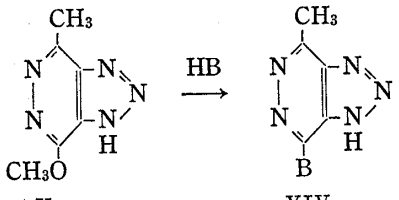
4-Methoxy-*v*-triazolo[4,5-*d*]pyridazine (Xb) was hydrolyzed to 4-hydroxy-compound (Xd) by just recrystallization from water, and this methoxyl group is readily replaced with various amines as chloro and alkylthio groups. Treatment of 3,6-dichloro-4,5-diaminopyridazine (Im) with sodium nitrite in diluted acetic acid solution gave 4-chloro-7-hydroxy-*v*-triazolo-[4,5-*d*]pyridazine (Xj) in 70% yield. Compound Xj was hydrogenated to compound Xd by treatment with hydrogen over palladium on charcoal.

There are two possible way in cyclization of 6-chloro-3,4,5-triaminopyridazine (Ik), the structure of reaction product Xk was determined following method. Dechlorination of Xk gave amino-triazolopyridazine which was identified with 4-amino-*v*-triazolo[4,5-*d*]pyridazine (XI) by comparison of infrared spectra. Compound XI was prepared from Xb by treatment with 28% ammonium hydroxide in a sealed tube.

Reaction of 4-Alkoxy-*v*-triazolo[4,5-*d*]pyridazines with Various Amines

Reaction of 4-methoxy-7-methyl-*v*-triazolo[4,5-*d*]pyridazine (Xg) with various amines gave corresponding 4-substituted amino-compounds in about 60% yield. Results were summarized in Table III.

Table III.

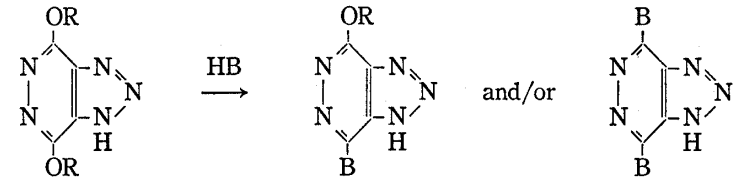


Xg XIV

HB (amines)	Reaction temp. (°C)	Reaction time (hr)	No.	mp (°C)	Yield (%)	Appearance[a]	Recryst. solvent
NH_3	160[b]	6	XIVa	>300	58	C.C.	NaOH–HCl
NH_2NH_2[c]	reflux	2	XIVb	290—291[d]	90	C.S.	water
$C_6H_5CH_2NH_2$[c]	130[b]	3	XIVc	>300	65	C.N.	MeOH
$HOCH_2CH_2NH_2$[c]	140[b]	3	XIVd	285—287[d]	60	C.N.	MeOH
$C_6H_{11}NH_2$[c]	140[b]	3	XIVe	>300	60	C.N.	EtOH
$(CH_3)_2NH$[c]	130[b]	3	XIVf	>300	73	C.N.	MeOH
piperidine[c]	140[b]	3	XIVg	263—265[d]	45	C.N.	MeOH

a) C: colorless, C: crystals, S: scales, N: needles *b*) sealed tube
c) methanolic solution *d*) decomp.

TABLE IV.



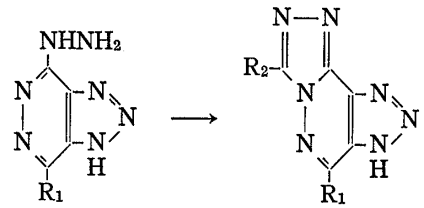
XV R=CH_3 XVI R=CH_3 XVIII
Xn R=C_2H_5 XVII R=C_2H_5

Start. mater.	HB (amines)	Reaction temp. (°C)	Reaction time (hr)	Products No.	mp (°C)	Yield (%)	Appear-ance[a]	Recryst. solv.
XV	NH_2NH_2[b]	reflux	3.5	XVIb	177.5—178.5[c]	82	C.N.	water
XV	$HOCH_2CH_2NH_2$	100	10	XVId	205.5—206.5	60	C.N.	MeOH
				XVIIId	252 —253	3.8	C.N.	MeOH
Xn	$C_6H_5CH_2NH_2$[d]	100[e]	7	XVIIc	220 —223	41	C.N.	EtOH
Xn	$HOCH_2CH_2NH_2$[d]	100[e]	2	XVIId	227 —230	33	C.N.	methyl cellosolve
XV	piperidine[b]	100[e]	4	XVIg	211 —212.5	30	C.N.	MeOH
XV	morpholine[b]	reflux	2	XVIh	246.5—247[c]	26	C.N.	MeOH-water
XV	morpholine[b]	100[e]	5	XVIIIh	>320	20	C.S.	MeOH-water
XVIh	morpholine[d]	reflux	10	XVIIIh	>320	18	C.S.	EtOH

a) C:colorless, N:needles, S:scales *b*) methanolic solution *c*) decomp.
d) ethanolic solution *e*) sealed tube

In case of reaction of 4,7-dialkoxy-*v*-triazolo[4,5-*d*]pyridazines with amines gave 4-substituted amino-7-alkoxy-*v*-triazolo[4,5-*d*]pyridazines accompanied with 4,7-di(substituted amino)-*v*-triazolo[4,5-*d*]pyridazines as by-products. Treatment of 4,7-dimethoxy-*v*-triazolo-[4,5-*d*]pyridazine (XV) with hydrazine hydrate gave 4-hydrazino-7-methoxy-*v*-tirazolo[4,5-*d*]-pyridazine (XVIb) as sole product. The reaction of XV with 2-hydroxyethylamine led to 4-(2-hydroxyethylamino)-7-methoxy-(XVId) and 4,7-di(2-hydroxyethylamino)-*v*-triazolo[4,5-*d*]pyridazine (XVIIId). Treatment of XV with morpholine gave 4-morpholino-7-methoxy-*v*-triazolo[4,5-*d*]pyridazine (XVIh) refluxing in methanol solution for 2 hours, though reaction in a sealed tube at 100°, 4,7-dimorpholino-compound (XVIIIh) was obtained as sole product in 20% yield.

New ring system, *s*-triazolo[4,3-*d*]-*v*-triazolo[4,5-*d*]pyridazines (XIX, XX), were synthesized by reaction of XIVb and XVIb with formic acid. Similarly, 4,7-dimethyl-compound (XXI) was obtained, when XIVb was treated with acetic anhydride. Kuwabara, *et al.* pointed out that unsubstituted *v*-triazolo[4,5-*d*] pyridazines at 1 or 3-position are acidity.[7] The new ring system compounds dissolved in aqueous 10% sodium carbonate solution, so we suggested those structure.



XIVb : R_1=CH_3 XIX: R_1=CH_3 R_2=H
XVIb : R_1=CH_3O XX: R_1=CH_3O R_2=H
XXI: R_1=CH_3 R_2=CH_3

Chart 3

Synthesized compounds were examined in photo stabilizing effect, some of *v*-triazolo [4,5-*d*]pyridazines showed good stabilizing effect.[7]

7) Y. Kuwabara, S. Irie, S. Sugita, M. Yanai, S. Takeda and H. Sadaki, *Nippon Shashingaku Kaishi*, **31**, 74 (1968).

Experimental

Imidazo[4,5-*d*]pyridazine (IIa)——A mixture of 0.41 g of Ia and 17 ml of 90% formic acid was refluxed for 12 hours, evaporated to dryness *in vacuo*. The residue was recrystallized.

4-Methoxyimidazo[4,5-*d*]pyridazine (IIb)——A mixture of 0.2 g of Ib, 2 ml of ethyl orthoformate and 2 ml of acetic anhydride was refluxed (crystals separated). After cool, the crystals were collected, recrystallized to give IIb. The mother liquor of reaction mixture was evaporated to dryness *in vacuo*. The residue was recrystallized from water to give a small quantity of colorless needles, mp>340°. This compound was identified with an authentic specimen of IId by infrared comparison.

4-Hydroxyimidazo[4,5-*d*]pyridazine (IId)——i) IIi (0.25 g) in 30 ml of 1% NaOH was hydrogenated over 0.3 g of 25% Pd–C. The catalyst was removed, the filtrate was acidified with diluted HCl, separated crystals were collected, recrystallized from water to give 0.19 g (95%) of colorless needles, mp>340° which was identified with an authentic sample of IId by infrared comparison.

ii) A mixture of 0.3 g of IIe and 10 ml of 28% ammonium hydroxide was heated at 190—200° for 25 hours in a sealed tube, evaporated to dryness *in vacuo*. The residue was recrystallized from water to give 0.17 g (70%) of colorless needles, mp>340°. This compound was identified with an authentic sample of IId by infrared comparison.

4-Methylthioimidazo[4,5-*d*]pyridazine (IIe)——To a solution of IIf and 4.4 ml of 10% KOH, 0.75 g of MeI was added, shaked violently for 30 minutes, allowed put in a refrigerator for overnight. The mixture was heated at 70—80° for 10 minutes. After cool, separated crystals were collected, recrystallized from MeOH to give 0.2 g (23%) of pale yellow prisms, mp 229—231° which was identified with an authentic sample of IIe by mixed melting point test and infrared comparison.

4-Mercaptoimidazo[4,5-*d*]pyridazine (IIf)——To a mixture of 0.5 g of IId and 50 ml of dry pyridine, 2.5 g of P_2S_5 was added. The mixture was refluxed for 10 hours, evaporated to dryness. To the residue, 80 ml of water was added, heated in a boiling water bath. After filtration, the filtrate was concentrated, separated crystals were collected, recrystallized from water to give 0.36 g (64%) of pale yellow needles, mp>320° which was identified with an authentic sample of IIf by infrared comparison.

4-Ethoxy-7-methylimidazo[4,5-*d*]pyridazine (IIh)——A solution of 0.18 g of IIIh and 50 ml of absolute EtOH was refluxed with 0.5 g of Raney nickel for 4 hours. Raney nickel was removed, the filtrate was evaporated to dryness, recrystallized from MeOH to give 81 mg of colorless needles. This compound was identified with an authentic sample of IIh by infrared comparison.

4-Hydroxy-7-methylimidazo[4,5-*d*]pyridazine (IIi)——A mixture of 0.4 g of I g and 3 ml of formamide was refluxed for 35 minutes. To the reaction mixture 5 ml of water was added, separated crystals were collected, recrystallized.

Table V

Compound No.	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
IIa	$C_5H_4N_4$	50.00	3.36	46.64	49.55	3.30	46.53
IIb	$C_6H_6ON_4$	48.00	4.03	37.32	48.02	4.22	36.91
IId	$C_5H_4ON_4$	44.12	2.96	41.16	44.42	3.01	40.81
IIe	$C_6H_6N_4S$	43.38	3.64	33.73	43.50	3.63	33.41
IIf	$C_5H_4N_4S$	39.46	2.65	36.82	39.54	2.64	36.50
IIg	$C_7H_8ON_4$	51.21	4.91		50.94	5.12	
IIh	$C_8H_{10}ON_4 \cdot 1/2H_2O$	51.33	5.39		51.30	5.53	
IIi	$C_6H_6ON_4$	48.00	4.03	37.32	48.33	3.88	37.54
IIj	$C_5H_3ON_4Cl$	35.21	1.77	32.85	35.71	1.55	32.62
IXa	$C_7H_8ON_4$	51.22	4.88	34.15	50.99	4.85	34.19
IIIg	$C_7H_8ON_4S \cdot 2/3H_2O$	40.59	4.52	26.96	40.38	4.49	26.92
IIIh	$C_8H_{10}ON_4S \cdot H_2O$	42.09	5.30	24.55	42.43	5.30	24.66
IIIn	$C_9H_{12}O_2N_4S \cdot 1/3H_2O$	43.90	5.15	22.76	44.09	5.28	22.76
IXb	$C_7H_8ON_4S$	42.86	4.08	28.57	42.40	3.93	28.38

4,5-Diacetamidopyridazine (IV)——To 0.42 g of Ia, a mixture of 4.2 ml of ethyl orthoformate and 4.2 ml of acetic anhydride was added, the crystals dissolved at once, after a while white crystals separated. The mixture was refluxed for 1.25 hours, after cool the crystals were collected, recrystallized from MeOH to give

0.14 g (19%) of colorless, mp 247—248°. *Anal.* Calcd. for $C_8H_{10}O_2N_4$: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.32; H, 5.18; N, 29.02.

Reaction of 4,5-Diamino-6-methyl-3(2*H*)pyridazinone (Ii) with Acetic Anhydride——A mixture of 2.9 g of Ii and 45 ml of acetic anhydride was refluxed for 2.5 hours, evaporated to dryness *in vacuo*. To the residue several ml of water was added, evaporated to dryness *in vacuo*. The residue was dissolved in MeOH, insoluble crystals were filtered, the filtrate was concentrated to give 3.85 (82%) of colorless prisms, mp 235—236.5° (melt this temperature, then solidified). *Anal.* Calcd. for $C_9H_{12}O_3N_4$ (VI): C, 48.21; H, 5.39; N, 24.99. Found: C, 48.01; H, 5.59; N, 24.63. The insoluble crystals were recrystallized from EtOH–water mixture to give 0.25 g (8%) of colorless prisms, mp>300°. *Anal.* Calcd. for $C_7H_8ON_4$ (VII): C, 51.21; H, 4.91; N, 34.13. Found: C, 51.21; H, 4.97; N, 33.95. This compound was also obtained following method; 0.5 g of VI was heated at 250—260°. Resultant solid was recrystallized from 60% EtOH to give 0.3 g (80%) of colorless prisms, mp>300°. *Anal.* Found: C, 51.21; H, 5.06; N, 34.13.

***v*-Triazolo[4,5-*d*]pyridazine (Xa)**——To a solution of 0.33 g of Ia and 20 ml of 10% acetic acid, $NaNO_2$ aq. solution (0.42 g in 5 ml of water) was added dropwise at 3—5° with stirring, after a while crystals separated. After 30 minutes, temperature was elevated to 70—80°, kept for 20 minutes. The mixture was evaporated to dryness *in vacuo*, the residue was dissolved in a small amount of water, acidified with 10% HCl. The separated crystals were filtered.

4-Hydroxy-*v*-triazolo[4,5-*d*]pyridazine (Xd)——i) Several times recrystallization of Xb from water gave Xd, mp 305—307° (decomp.) which was identified with an authentic sample by infrared comparison. ii) Xj (0.2 g) in 13 ml of 28% ammonium hydroxide was hydrogenated over 0.4 g of 20% Pd–C. The separated was removed, the filtrate was acidified with diluted HCl, concentrated under reduced pressure, catalyst crystals were collected, recrystallized from water to give a small quantity of pale yellow prisms, mp 305—307° (decomp.) which was identified with an authentic sample of Xd by infrared comparison.

Table VI

Compound No.	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
Xa	$C_4H_3N_5$	39.67	2.50	57.83	39.58	2.30	57.56
Xb	$C_5H_5ON_5$	39.74	3.33	46.34	39.70	3.31	46.49
Xd	$C_4H_3ON_5$	35.04	2.21	51.08	35.08	2.26	50.70
Xe	$C_5H_5N_5S$	35.92	3.01	41.89	35.73	2.92	41.48
Xf	$C_4H_3N_5S$	31.37	1.97	45.73	31.73	2.00	45.05
Xg	$C_6H_7ON_5 \cdot H_2O$	39.34	4.95	38.23	39.46	5.04	37.81
Xh	$C_7H_9ON_5$	46.92	5.06	39.08	47.10	5.17	39.04
Xi	$C_5H_5ON_5$	39.74	3.33	46.34	39.87	3.60	46.00
Xj	$C_4H_2ON_5Cl$	28.01	1.18	40.83	28.27	0.99	40.28
Xk	$C_4H_3N_6Cl$	28.17	1.77	49.27	28.22	1.76	48.99
Xn	$C_8H_{11}O_2N_5$	45.93	5.30	33.48	45.72	5.22	33.16
Xp	$C_6H_7O_2N_5$	39.78	3.89	38.66	40.01	3.86	38.53

4-Amino-*v*-triazolo[4,5-*d*]pyridazine (XI)——i) A mixture of 0.3 g of Xb and 10 ml of 28% ammonium hydroxide was heated at 160—165° for 5.5 hours in a sealed tube. The reaction mixture was concentrated, separated crystals were recrystallized from diluted ammonium hydroxide to give 0.16 g (60%) of thin needles, mp>300°. *Anal.* Calcd. for $C_4H_4N_6$: C, 35.29; H, 2.96; N, 61.75. Found: C, 35.57; H, 3.04; N, 61.91.

ii) Xh (0.25 g) in 30 ml of 2% ammonium hydroxide was hydrogenated over 0.3 g of 10% Pd–C. The catalyst was filtered, the filtrate was evaporated to dryness *in vacuo*. The residue was recrystallized from diluted ammonium hydroxide to give 0.17 g (80%) of thin needles, mp>300°. *Anal.* Found: C, 35.04; H, 3.18; N, 61.44. This compound was identified with an authentic sample of XI by infrared comparison.

4-Amino-7-methyl-*v*-triazolo[4,5-*d*]pyridazine (XIVa)——A mixture of 0.5 g of Xg and 15 ml of 28% ammonium hydroxide was heated at 160° for 6 hours in a sealed tube. The reaction mixture was concentrated to a small volume. The separated crystals were collected, dissolved in 0.5% NaOH solution, acidified with acetic acid. The separated crystals were filtered to give 0.24 g of XIVa. The acidic filtrate was evaporated to dryness, the residue was recrystallized from water which contained few drops of 10% HCl. Recrystallization from water gave 0.04 g (4%) of colorless prisms, mp 295—295.5° (decomp.). It was identified with an authentic sample of XIi by mixed melting point test and infrared comparison.

4-Hydrazino-7-methyl-*v*-triazolo[4,5-*d*]pyridazine (XIVb)——A mixture of 0.5 g of Xg, 6 ml of MeOH and 1 g of 80% hydrazine hydrate was refluxed for 2 hours. After cool, the separated crystals were filtered.

Table VII

Compound No.	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
XIVa	$C_5H_6N_6$	39.99	4.03	55.98	40.18	4.12	55.70
XIVb	$C_5H_7N_7$	36.36	4.27	59.37	35.96	4.46	59.16
XIVc	$C_{12}H_{12}N_6$	59.98	5.03	34.98	60.24	5.25	35.02
XIVd	$C_7H_{10}ON_6$	43.29	5.19	43.28	43.47	5.36	43.51
XIVe	$C_{11}H_{16}N_6$	56.89	6.90	36.20	56.60	6.84	36.31
XIVf	$C_7H_{10}N_6$	47.18	5.66	47.17	46.95	5.85	46.99
XIVg	$C_{10}H_{14}N_6$	55.03	6.47	38.51	55.33	6.70	38.25
XVIb	$C_5H_7ON_7 \cdot H_2O$	30.15	4.55	49.23	30.00	4.37	48.84
XVId	$C_7H_{10}O_2N_6$	40.00	4.80	39.98	40.00	4.84	39.77
XVIIc	$C_{13}H_{14}ON_6$	57.76	5.22	31.11	57.59	5.22	30.88
XVIId	$C_8H_{12}O_2N_6$	42.85	5.39	37.48	42.58	5.50	37.72
XVIg	$C_{10}H_{14}ON_6$	51.27	6.02	35.88	51.43	6.16	35.88
XVIh	$C_9H_{10}O_2N_6$	45.76	5.12	35.58	46.04	5.15	35.48
XVIIId	$C_8H_3O_2N_7 \cdot 1/2H_2O$	38.71	5.68	39.50	38.80	5.80	39.40
XVIIIh	$C_{12}H_{17}O_2N_7$	49.48	5.88	33.65	49.79	6.00	33.78

Hydrochloride of XVb was recrystallized from EtOH to give colorless needles, mp 250° (decomp.). *Anal.* Calcd. for $C_5H_7N_7 \cdot HCl$: C, 29.83; H, 3.97; N, 48.63. Found: C, 30.11; H, 4.04; N, 48.91.

4,7-Dimorpholino-*v*-triazolo[4,5-*d*]pyridazine (XVIIIh)——i) A mixture of 0.3 g of XVIh, 0.5 g of morpholine and 20 ml of EtOH was refluxed for 10 hours. After cool, separated crystals were collected, recrystallized from EtOH to give 0.08 g (18%) of colorless scales, mp >320°. This compound was identified with an authentic sample of XVIIIh by infrared comparison.

4-Methyl-*s*-triazolo[4,3-*d*]-*v*-triazolo[4,5-*d*]pyridazine (XIX)——A mixture of 0.2 g of XIVb and 10 ml of formic acid was refluxed for 2 hours. The reaction mixture was evaporated to dryness *in vacuo*, the residue was recrystallized from MeOH to give 0.16 g (80%) of colorless prisms, mp 270—273° (decomp.). *Anal.* Calcd. for $C_6H_5N_7$: C, 41.14; H, 2.88; N, 55.98. Found: C, 41.05; H, 2.77; N, 55.96.

4-Methoxy-*s*-triazolo[4,3-*d*]-*v*-triazolo[4,5-*d*]pyridazine (XX)——A mixture of 0.3 g of XVIb and 2 ml of formic acid was refluxed for 2 hours. The reaction mixture was evaporated to dryness *in vacuo*. The residue was recrystallized from MeOH to give 0.21 g (72%) of colorless plates, mp 206.5° (decomp.). *Anal.* Calcd. for $C_6H_5ON_7$: C, 37.70; H, 2.64; N, 51.29. Found: C, 38.00; H, 2.62; N, 51.45.

4,7-Dimethyl-*s*-triazolo[4,3-*d*]-*v*-triazolo[4,5-*d*]pyridazine (XXI)——A mixture of 0.25 g of XIVb and 7 ml of acetic anhydride was refluxed for 2 hours. The reaction mixture was evaporated to dryness *in vacuo*, the residue was recrystallized from MeOH to give 0.2 g (80%) of pale yellow prisms, mp 318° (decomp.). *Anal.* Calcd. for $C_7H_7N_7$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.44; H, 3.89; N, 51.93.

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