washed with H_2O, and dried to 0.35 g. of white needles, m.p. 288~289°(decomp.). *Anal.* Calcd. for $C_{12}H_{10}N_8S_3$: C, 39.78; H, 2.87. Found: C, 39.98; H, 3.01.

5-Amino-7-methylthio-*s*-triazolo[2,3-*a*]pyrimidine (XXIV)——a) A mixture of 2.0 g. of (XXI) and 30 cc. of EtOH-NH_3 was heated in a sealed tube at 150~160° for 10 hr. The reaction mixture was evaporated to dryness, the residue wes dissolved in dil. HCl, filtered with charcoal, and the filtrate was neutralized with dil. NaOH to form 1.3 g. of white crystalline product. Recrystallization from EtOH gave colorless needles, m.p. 230~231°. *Anal.* Calcd. for $C_6H_7N_5S$: C, 39.77; H, 3.89; N, 38.65. Found: C, 40.06; H, 4.18; N, 38.58.

b) A mixture of 0.4 g. of (X) and 15 cc. of EtOH-NH_3 was reacted as above and the product was recrystallized from EtOH to 0.35 g. of colorless needles, m.p. 230~231°, which showed no depression on admixture with (XXIV), prepared by the method (a).

The author is deeply grateful to Dr. K. Takeda, Director of this Laboratory, and to Dr. H. Kanō of this Laboratory, for their helpful guidance and encouragement. Thanks are also due to Messrs. H. Miyazaki and I. Tanaka for ultraviolet and infrared spectral measurements, and to the members of the Analysis Room of this Laboratory for elemental analysis.

Summary

The products of the condensation of 5-amino-*s*-triazole (I) with ethyl malonate, ethyl cyanoacetate, and methyl ethoxycarbonyldithioacetate were proved to be respectively 5,7-dihydroxy-, 5-hydroxy-7-amino-, and 5-hydroxy-7-mercapto-*s*-triazolo[2,3-*a*]pyriminines (II, III, and IV). (II) was converted into the 5,7-dichloro derivative (VI), and the reactivity of the two halogens in (VI) towards the usual nucleophilic reagents was examined. (IV) was also transformed into the 5-chloro-7-methylthio derivative (XXI), which was converted into 5-substituted 7-methylthio derivatives by nucleophilic substitution. Ultraviolet absorption spectra of 5-substituted and 7-substituted *s*-triazolo[2,3-*a*]pyrimidines were compared.

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126. Yasuo Makisumi: Synthesis of Potential Anticancer Agents. V.*2 6-Halo-*s*-triazolo[2,3-*a*]pyrimidines.

(*Research Laboratory, Shionogi & Co., Ltd.**1)

In the previous paper[1] of this series, it was reported that the reaction of 5-methyl-7-hydroxy-*s*-triazolo[2,3-*a*]pyrimidine (I) with phosphoryl chloride gave 5-methyl-7-chloro derivative (II), but that the reaction of (I) with a mixture of phosphorus pentachloride and phosphoryl chloride resulted in the formation of the 5-methyl-6,7-dichloro derivative (IIa). In the latter reaction, it was assumed that the 6-position of (I) was activated for electrophilic substitution by the hydroxyl group at 7-position and consequently was chlorinated with phosphorus pentachloride into the 5-methyl-6-chloro-7-hydroxy derivative (Ia) and then chlorination of the hydroxyl group of (Ia) followed to give (IIa). In order to prove this assumption, the halogenation of 7-hydroxy- or 7-amino-*s*-triazolo[2,3-*a*]pyrimidine and its 5-methyl derivative with chlorine or bromine was carried out, and the expected 6-halo derivatives were obtained.[1,2]

*1 Fukushima-ku, Osaka (牧角徳夫).

*2 Part IV: This Bulletin, **9**, 801 (1961).

1) H. Kanō, Y. Makisumi, S. Takahashi, M. Ogata: *Ibid.*, **7**, 903 (1959).

2) Y. Makisumi, H. Kanō: *Ibid.*, **7**, 907 (1959).

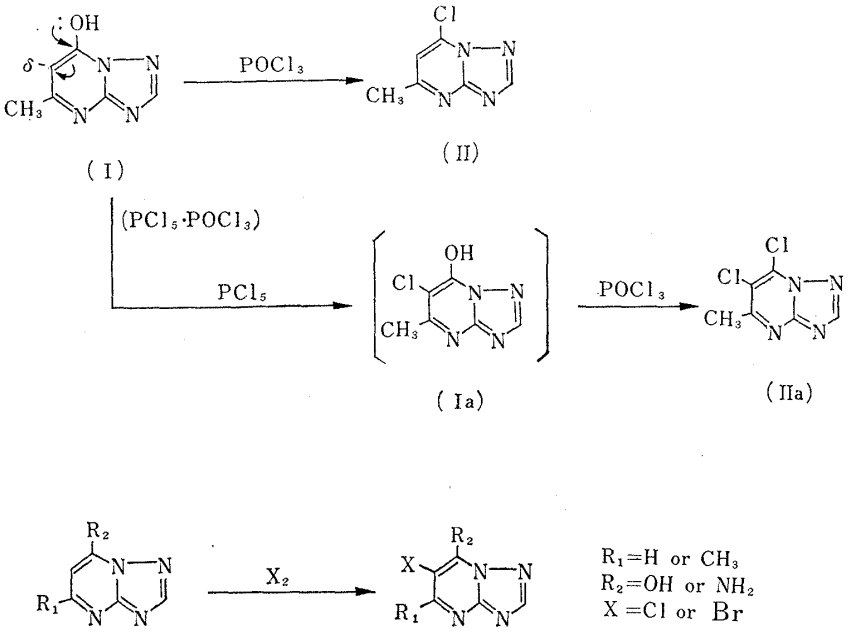


Chart 1.

The present study deals with the halogenation of the derivatives of *s*-triazolo[2,3-*a*]-pyrimidine, and the direct synthesis of 6-halo-*s*-triazolo[2,3-*a*]pyrimidines.

s-Triazolo[2,3-*a*]pyrimidine (III) and its 5-methyl derivative (IV) were halogenated by the action of chlorine or bromine in glacial acetic acid at room temperature to corresponding monohalogenated products (IIIa, IIIb, IVa, and IVb). These compounds were identical with 6-halo- and 5-methyl-6-halo-*s*-triazolo[2,3-*a*]pyrimidines which were obtained by catalytic reduction of 6-halo-7-chloro-*s*-triazolo[2,3-*a*]pyrimidines[2] (Va and Vb) and their 5-methyl derivatives[1] (IIa and IIb). However, 5,7-dimethyl-*s*-triazolo[2,3-*a*]pyrimidine[3] (VI) did not react with chlorine or bromine under the same condition.

These experiments suggest that the reaction proceeds by the following mechanism. In the *s*-triazolo[2,3-*a*]pyrimidine (III) and its 5-methyl derivative (IV), their 6-positions are activated towards electrophilic substitution by the —M effect of the ring-nitrogen at the 8-position and therefore (III) and (IV) were halogenated into 6-halogen derivatives (IIIa, IIIb, IVa, and IVb), while no reaction occurred in the 5,7-dimethyl derivative (VI), owing to steric hindrance of the two methyl groups.

Reaction of 5-hydroxy-7-amino derivative*[2] (VII) and 5,7-dihydroxy derivative*[2] (VIII) with bromine in glacial acetic acid gave 6-bromo derivatives (VIIa and VIIIb) but the reaction of (VII) and (VIII) with chlorine did not produce 6-chloro derivatives (VIIa and VIIIa), resulting in the formation of a substance, $C_4H_4ON_4Cl_2$, m.p. 217° (decomp.) (IX), and half of the original materials (VII and VIII) was recovered. (IX) was identified with 5-dichloroacetamido-*s*-triazole obtained by reaction of 5-amino-*s*-triazole (X) with dichloroacetyl chloride. In this reaction, the use of two moles of chlorine for (VII) and (VIII) gave (IX) in a good yield without recovery of the original materials (VII and VIII).

These abnormal reactions seem to be the result of the following mechanism. 6-Position of (VII) or (VIII) is strongly activated by the two adjacent hydroxyl or amino groups which could take keto and imino form (VII′ and VIII′), so that the chlorination gave 6,6-dichloro derivatives (VIIc and VIIIc), replacing the two hydrogen atoms at 6-position. Ring cleavage between 7- and 8-position to (XI) and subsequent decomposition of (XI) would produce (IX). On the other hand, in the case of bromination of (VII) and (VIII), the replace-

3) C. Bülow, K. Haas : Ber., **42**, 4638 (1909); K. Shirakawa : Yakugaku Zasshi, **79**, 903 (1959).

ment of two atoms of bromine at 6-position could not occur due to a large volume of the bromine atom and 6-bromo derivatives (VIIIb and VIIIb) were obtained in a good yield.

Thus, it was clarified that the 6-position of *s*-triazolo[2,3-*a*]pyrimidines is readily halogenated with chlorine or bromine, except in a few cases.

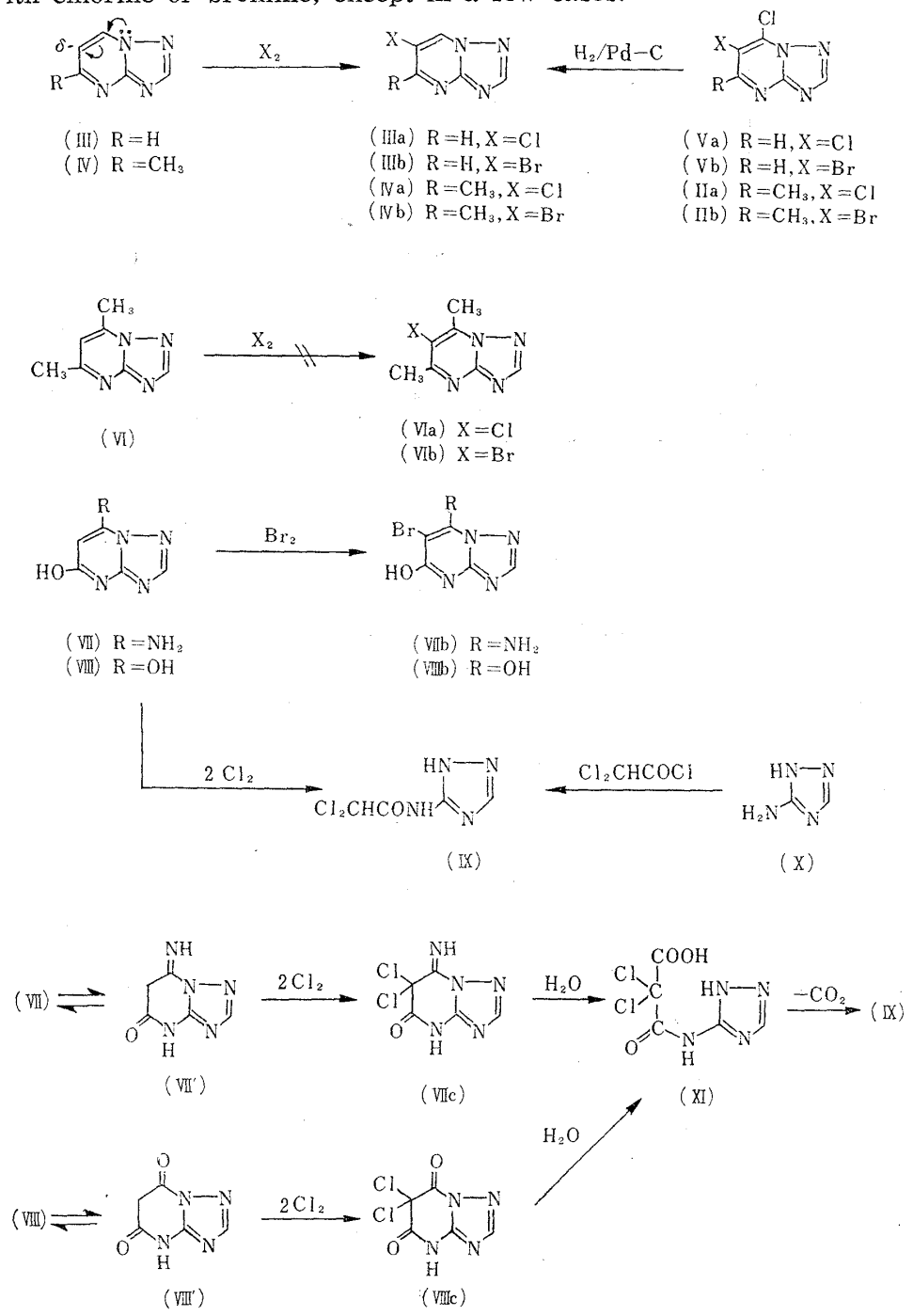


Chart 2.

It was also reported in the previous paper[1] that the condensaton of ethyl 2-haloacetoacetate with (X) gave 5-methyl-6-halo-7-hydroxy-*s*-triazolo[2,3-*a*]pyrimidines (Ia and Ib). Attempts to synthesize 5,7-disubstituted 6-halo-*s*-triazolo[2,3-*a*]pyrimidines were carried out by the same method.

Treatment of 3-halopentane-2,4-dione with (X) in ethanol at boiling temperature for 8 hours gave 5,7-dimethyl-6-chloro-*s*-triazolo[2,3-*a*]pyrimidine (VIa) in a good yield, but

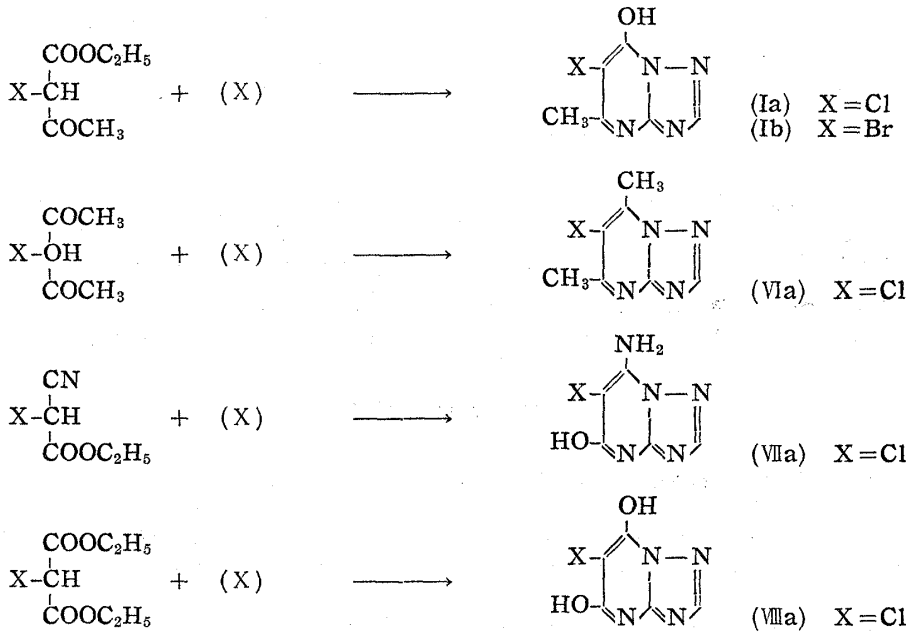
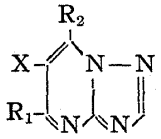


Chart 3.

TABLE I. Ultraviolet Absorption Spectra of 6-Halo-*s*-triazolo[2,3-*a*]pyrimidines



Compd. No.	R_1	R_2	X	λ_{max}^{EtOH} mμ (log ε)		Δλ (mμ)
(III)	H	H	H		273 (3.57)	
(IIIa)	〃	〃	Cl		290 (3.54)	+17
(IIIb)	〃	〃	Br		291.5 (3.51)	+18.5
(IV)	CH_3	〃	H		272 (3.59)	
(IVa)	〃	〃	Cl		286 (3.58)	+14
(IVb)	〃	〃	Br		288 (3.59)	+16
(II)	〃	Cl	H		275 (3.71)	
(IIa)	〃	〃	Cl		288 (3.68)	+13
(IIb)	〃	〃	Br		291 (3.70)	+16
(VI)	〃	CH_3	H		271 (3.70)	
(VIa)	〃	〃	Cl		284.5 (3.66)	+13.5
(VII)	OH	NH_2	H		269 (4.13)	
(VIIa)	〃	〃	Cl		277.5 (4.07)	+8.5
(VIIb)	〃	〃	Br		279 (4.07)	+10
(VIII)	〃	OH	H		261 (4.14)	
(VIIIa)	〃	〃	Cl		273 (4.11)	+12
(VIIIb)	〃	〃	Br		273.5 (4.03)	+12.5
	H	NH_2	H	263.5 (3.72) *a)*	292 (4.10)	
	〃	〃	Cl	261 (3.69)	304 (4.05)	+12
	〃	〃	Br	262 (3.72)	304 (4.03)	+12
	CH_3	〃	H	258 (3.71) *a)*	287 (4.10)	
	〃	〃	Cl	260 (3.66)	298 (4.02)	+11
	〃	〃	Br	261 (3.66)	297.5 (3.99)	+10.5
	H	OH	H	242 (3.67)	274 (3.96)	
	〃	〃	Cl	251 (3.72)	293.5 (3.95)	+19.5
	〃	〃	Br	252.5 (3.74)	295.5 (3.95)	+21.5
	CH_3	〃	H	240 (3.62) *a)*	272 (4.02)	
	〃	〃	Cl	251.5 (3.69)	289 (3.98)	+17
	〃	〃	Br	252.5 (3.73)	290.5 (3.98)	+18.5

a) shoulder

the 6-bromo derivative (VIb) was not obtained owing to resinification. Ethyl halocyanoacetate and ethyl halomalonate similarly reacted with (X) in the presence of sodium ethoxide in ethanol to give 5-hydroxy-6-chloro-7-amino derivative (VIIa) and 6-chloro-5,7-dihydroxy derivative (VIIIa), both in a poor yield, but 6-bromo derivatives (VIIb and VIIIb) were not obtained owing to resinification.

Ultraviolet absorption spectra of 6-halo-*s*-triazolo[2,3-*a*]pyrimidines were measured. These spectra showed similar curves to the spectra of the corresponding original compounds and the introduction of halogen at 6-position produced a bathochromic shift to the extent of about 10~20 mμ and a little hypochromic effect.

Biological details of these compounds will be published elsewhere.

Experimental*3

6-Chloro-*s*-triazolo[2,3-*a*]pyrimidine (IIIa)——a) To a solution of 1.2 g. of (III) in 12 cc. of AcOH, 0.7 g. of Cl_2 was absorbed. After stirring at room temperature for 3 hr., the solvent was evaporated to dryness in a reduced pressure and the residue was recrystallized from H_2O to 0.9 g. of colorless needles, m.p. 174~175°. *Anal.* Calcd. for $C_5H_3N_4Cl$: C, 38.87; H, 1.97; N, 36.27. Found: C, 38.99; H, 2.22; N, 36.15.

b) To a solution of 0.45 g. of 6,7-dichloro-*s*-triazolo[2,3-*a*]pyrimidine (Va) in 45 cc. of dehyd. EtOH, 0.2 g. of 5% Pd-C and 0.2 g. of Na_2CO_3 were added and the mixture was shaken at room temperature in H_2 stream. A theoretical uptake of 1 mole of H_2 occurred during about 1 hr. After removal of the catalyst, the filtrate was evaporated to dryness, 10 cc. of H_2O was added to the residue, and the insoluble crystals were collected and recrystallized from H_2O to 0.35 g. of colorless needles, m.p. 174~175°, alone and in admixture with the sample prepared by method (a). *Anal.* Calcd. for $C_5H_3N_4Cl$: C, 38.87; H, 1.97; N, 36.27. Found: C, 39.24; H, 2.09; N, 36.26.

6-Bromo-*s*-triazolo[2,3-*a*]pyrimidine (IIIb)——a) To a solution of 0.6 g. of (III) in 6 cc. of AcOH, 0.8 g. of Br_2 in 4 cc. of AcOH was added in drops with stirring. After stirring for 3 hr., the solvent was evaporated *in vacuo* and the residue was recrystallized from H_2O to 0.6 g. of colorless pillars, m.p. 183~184°. *Anal.* Calcd. for $C_5H_3N_4Br$: C, 30.17; H, 1.52; N, 28.45. Found: C, 30.50; H, 1.81; N, 28.21.

b) To a solution of 1 g. of 6-bromo-7-chloro-*s*-triazolo[2,3-*a*]pyrimidine (Vb) in 100 cc. of dehyd. EtOH, 0.4 g. of Na_2CO_3 and 0.4 g. of 5% Pd-C were added and the mixture was submitted to reduction at ordinary temperature and pressure. After 1 mole of H_2 was absorbed, the reaction mixture was treated by the same method as for (IIIa) in (a) and the resulting product was recrystallized from H_2O to 0.5 g. of colorless pillars, m.p. 183~184°, alone and in admixture with the sample (IIIb) prepared by the method (a).

5-Methyl-6-chloro-*s*-triazolo[2,3-*a*]pyrimidine (IVa)——To a solution of 1.34 g. of (IV) in 20 cc. of AcOH, 0.7 g. of Cl_2 was absorbed. After stirring at room temperature for 3 hr., the solvent was evaporated to dryness in a reduced pressure, the residue was basified with dil. NH_4OH, extracted with $CHCl_3$, and dried over Na_2SO_4. The extract was evaporated and the resulting crystals were recrystallized from ligroine to 1.3 g. of colorless pillars, m.p. 130~131°, alone and in admixture with the authentic sample of (IVa).[1] *Anal.* Calcd. for $C_6H_5N_4Cl$: C, 42.74; H, 2.98; N, 33.23. Found: C, 43.02; H, 3.29; N, 33.17.

5-Methyl-6-bromo-*s*-triazolo[2,3-a]pyrimidine (IVb)——a) To a solution of 1.34 g. of (IV) in 20 cc. of AcOH, a solution of 1.6 g. of Br_2 in 10 cc. of AcOH was added dropwise with stirring. After stirring for further 3 hr., the reaction mixture was treated by the same method as for (IVa) and the resulting product was recrystallized from ligroine to 1.5 g. of colorless pillars, m.p. 137~138°. *Anal.* Calcd. for $C_6H_5N_4Br$: C, 33.82; H, 2.36; N, 26.29; Br, 37.50. Found: C, 34.17; H, 2.57; N, 26.05; Br, 37.30.

b) To a solution of 1.24 g. of 5-methyl-6-bromo-7-chloro-*s*-triazolo[2,3-*a*]pyrimidine (IIb) in 100 cc. of dehyd. EtOH, 0.3 g. of 5% Pd-C was added and the mixture was reduced under the same condition as above. After 1 mole of H_2 was absorbed, the reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was basified with dil. NH_4OH and extracted with $CHCl_3$, which was dried over Na_2SO_4. The solvent was evaporated and the resulting crystals were recrystallized from ligroine to 0.8 g. of colorless pillars, m.p. 137~138°, alone and in admixture with the sample (IVb) prepared by the method (a).

*3 All melting points are uncorrected. Ultraviolet spectra were measured with the Hitachi Recording Spectrophotometer, EPS-2.

5-Hydroxy-6-bromo-7-amino-*s*-triazolo[2,3-*a*]pyrimidine (VIIb)——To a suspension of 1.5 g. of 5-hydroxy-7-amino-*s*-triazolo[2,3-*a*]pyrimidine (VII) in 30 cc. of AcOH, a solution of 1.6 g. of Br_2 in 10 cc. of AcOH was added in drops with stirring and the reaction mixture was soon decolorized. After stirring at room temperature for further 1 hr., the resulting precipitate was collected, dissolved in dil. NaOH, filtered with charcoal, and the filtrate was acidified with dil. AcOH to 2.2g. of white crystals. Recrystallization from 50% MeOH gave colorless needles, m.p. above 320°. *Anal.* Calcd. for $C_5H_4ON_5Br$: C, 26.09; H, 1.74; N, 30.43. Found : C, 26.39; H, 1.85; N, 30.19.

5,7-Dihydroxy-6-bromo-*s*-triazolo[2,3-*a*]pyrimidine (VIIIb)——To a suspension of 3 g. of 5,7-dihydroxy-*s*-triazolo[2,3-*a*]pyrimidine (VIII) in 100 cc. of AcOH, a solution of 3.2 g. of Br_2 in 20 cc. of AcOH was added in drops. After stirring for 30 min., the separated crystals were collected, dissolved in dil. NaOH, filtered with charcoal, and the filtrate was acidified with HCl to 4 g. of white scales, m.p. above 320°. Recrystallization from H_2O gave colorless scales, m.p. above 320°. *Anal.* Calcd. for $C_5H_3O_2N_4Br \cdot \frac{1}{2}H_2O$: C, 25.00; H, 1.67; N, 23.33. Found : C, 24.88; H, 1.89; N, 23.10.

5-Dichloroacetamido-*s*-triazole (IX)——To a suspension of 3.4 g. of (X) in 90 cc. of dehyd. benzene, a solution of 9.2 g. of dichloroacetyl chloride in 10 cc. of benzene was added dropwise, the mixture was refluxed for 3 hr., and allowed to stand overnight. The insoluble part was collected by filtration and recrystallized from hydr. EtOH to 0.9 g. of white needles, m.p. 217°(decomp.). *Anal.* Calcd. for $C_4H_4ON_4Cl_2$: C, 24.63; H, 2.06; N, 28.73. Found : C, 24.90; H, 2.07; N, 28.65.

Reaction of (VII) with Cl_2——To a suspension of 1.5 g. of (VII) in 30 cc. of AcOH, 0.7 g. of Cl_2 was absorbed. After stirring for 2 hr. at room temperature, the insoluble portion was filtered off, the filtrate was evaporated to dryness in a reduced pressure, and the residue was recrystallized from hydr. EtOH to 0.7 g. of white needles (IX), m.p. 217°(decomp.). *Anal.* Calcd. for $C_4H_4ON_4Cl_2$: C, 24.63; H, 2.06; N, 28.73; Cl, 36.36. Found : C, 24.73; H, 2.03; N, 28.54; Cl, 36.40.

The insoluble portion was dissolved in dil. NaOH, filtered with charcoal, and the filtrate was acidified with AcOH, affording white crystals (0.7 g.), which were recrystallized from hydr. EtOH to colorless prisms, m.p. over 320°, identified with (VII) by infrared spectrum.

Reaction of (VIII) with Cl_2——To a suspension of 1.5 g. of (VIII) in 30 cc. of AcOH, 0.7 g. of Cl_2 was absorbed. The mixture was reacted and treated as above to 0.6 g. of white needles (IX), m.p. 217°(decomp.). *Anal.* Calcd. for $C_4H_4ON_4Cl_2$: C, 24.63; H, 2.06; N, 28.73. Found : C, 24.77; H, 2.26; N, 28.63.

The insoluble portion (0.65 g.) was recrystallized from hydr. EtOH to colorless needles, m.p. 238° (decomp.), which was identified with (VIII).

5,7-Dimethyl-6-chloro-*s*-triazolo[2,3-a]pyrimidine (VIa)——A solution of 5.4 g. of 3-chloropentene-2,4-dione and 3.3 g. of (X) in 15 cc. of EtOH was refluxed for 8 hr. The reaction mixture was concentrated to one-half the original volume, the resulting crystals were collected by filtration, and recrystallized from ligroine to 4.6 g. of colorless pillars, m.p. 101~102°. *Anal.* Calcd. for $C_7H_7N_4Cl$: C, 46.03; H, 3.86; N, 30.68. Found : C, 46.07; H, 4.13; N, 30.26.

5-Hydroxy-6-chloro-7-amino-*s*-triazolo[2,3-*a*]pyrimidine (VIIa)——To a solution of 1.5 g. of Na in 55 cc. of dehyd. EtOH, 7.3 g. of ethyl chlorocyanoacetate and 5.3 g. of (X) were added. The solution was refluxed for 3.5 hr. and colored brown, when the Na salt deposited. After cool, the resulting Na salt was collected by filtration, dissolved in H_2O, filtered with charcoal, and the filtrate was acidified with dil. AcOH to colored crystals. White needles (0.8 g.), m.p. above 320°, of (VIIa) were obtained after the precipitation was repeated. *Anal.* Calcd. for $C_5H_4ON_5Cl$: C, 32.35; H, 2.15; N, 37.74. Found : C, 32.78; H, 2.47; N, 37.34.

5,7-Dihydroxy-6-chloro-*s*-triazolo[2,3-*a*]pyrimidine (VIIIa)——To a solution of 0.8 g. of Na in 30 cc. of dehyd. EtOH, 6.5 g. of ethyl chloromalonate and 2.8 g. of (X) were added and the solution was refluxed for 6 hr. After cool, the precipitated Na salt was treated as above and the resulting product was recrystallized from hydr. EtOH to 0.5 g. of colorless needles, m.p. above 320°. *Anal.* Calcd. for $C_5H_3O_2N_4Cl \cdot \frac{1}{2}H_2O$: C, 30.50; H, 2.04; N, 28.68; Cl, 18.15. Found : C, 30.23; H, 2.43; N, 28.61; Cl, 17.92.

The author expresses his gratitude to Dr. K. Takeda, Director of this Laboratory, and to Dr. H. Kanō of this Laboratory, for their helpful guidance and encouragement. Ultraviolet spectra were measured by Dr. T. Kubota and Mr. I. Tanaka, and elemental analyses were carried out by the members of Analysis Room of this Laboratory, to all of whom the author is indebted.

Summary

Halogenation of *s*-triazolo[2,3-*a*]pyrimidine and its 5-methyl derivative with chlorine or bromine gave the corresponding 6-halo derivative (IIIa, IIIb, IVa, and IVb), but in the

case of 5-hydroxy-7-amino- and 5,7-dihydroxy-*s*-triazolo[2.3-*a*]pyrimidines, reaction of bromine gave 6-bromo derivatives (VIIb and VIIIb) while that of chlorine gave 5-dichloroacetamido-*s*-triazole (IX) instead of 6-chloro derivatives (VIIa and VIIIa). 2-Halo-1,3-dicarbonyl compounds were condensed with 5-amino-*s*-triazole (X) into 6-chloro-*s*-triazolo[2,3-*a*]pyrimidines (VIa, VIIa, and VIIIa), but 6-bromo derivatives were not obtained due to resinification. Ultraviolet spectra of 19 kinds of 6-halo-*s*-triazolo[2,3-*a*]pyrimidines were measured and compared with those of the corresponding original compounds.

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[127] **Yasuo Makisumi** : Synthesis of Potential Anticancer Agents. VI.*2
Reactivity of 6-Bromo-*s*-triazolo[2,3-*a*]pyrimidines.

(*Research Laboratory, Shionogi & Co., Ltd.**1)

In Part III of this series,[1] it was shown that the halogen atom at 7-position of *s*-triazolo[2,3-*a*]pyrimidines reacted readily with nucleophilic reagents, but the halogen atom at 6-position was very resistant to nucleophilic substitutions. For example, 6,7-dihalo-*s*-triazolo[2,3-*a*]pyrimidines reacted with acid or alkali, ammonia, thiourea, and hydrogen iodide to form 7-hydroxy-, 7-amino-, 7-mercapto-, and 7-iodo-6-halo-*s*-triazolo[2,3-*a*]-pyrimidines, respectively.

X=Cl or Br R=OH, NH_2, SH or I

It has been generally concluded that in the pyrimidine series halogens at 5-position of pyrimidines are quite stable and difficult to be displaced by nucleophilic reagents, except in a few cases.

However, Phillips[2] has reported that the 5-bromo derivatives of uracil and isocytosine react with several amines to give the corresponding 5-substituted amino derivatives. Barker and co-workers[3] have also reported that the 5-bromo derivatives of barbituric acid and 6-aminouracil react with thiourea to give the corresponding derivatives containing sulfur at their 5-position.

These facts suggested the possibility that, in *s*-triazolo[2,3-*a*]pyrimidines, the presence of groups capable of tautomerism at both 5- and 7-positions might activate the halogen at 6-position sufficiently to bring about a reaction. In order to clarify this point, the same reactions were carrried out with 6-bromo-*s*-triazolo[2,3-*a*]pyrimidines in the present series of work.

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*1 Fukushima-ku, Osaka (牧角徳夫).
*2 Part V : This Bulletin, **9**, 808 (1961).
1) Y. Makisumi, H. Kanō : *Ibid.*, **7**, 907 (1959).
2) A.P. Phillips : J. Am. Chem. Soc., **73**, 1061 (1951); *ibid.*, **75**, 4092 (1953).
3) G.R. Barker, N.G. Luthy, M.M. Dhar : J. Chem. Soc., **1954**, 4206.