UDC 547.859.3.07

147. Yasuo Makisumi : Studies on Azaindolizine Compounds. XV.*2 The Allyl Rearrangement of 5-Methyl-7-allyloxy-*s*-triazolo[1,5-*a*]pyrimidine.

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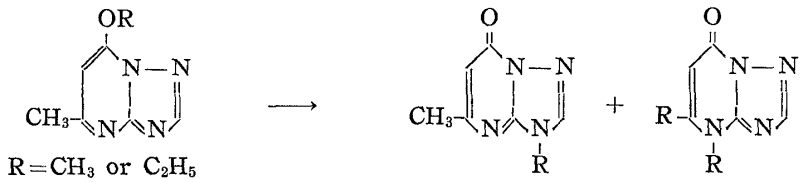
In a previous work[1] of this series, it was discovered that the thermal rearrangement*3 of 5-methyl-7-alkoxy-*s*-triazolo[1,5-*a*]pyrimidines afforded 3- and 4-alkyl-5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H* and 4*H*)-ones by the migration of the alkyl group to the ring nitrogens at the 3- and 4-positions.



Generally, it has been well-known as Claisen rearrangement[2] that the allyl group of the aromatic allylic ethers migrates to its *ortho*-position by heating.

In connection with these rearrangement reactions, the thermal behavior of 5-methyl-7-allyloxy-*s*-triazolo[1,5-*a*]pyrimidine (II) has been now investigated.

The starting material (II) was prepared by the reaction of 5-methyl-7-chloro-*s*-triazolo[1,5-*a*]pyrimidine (I) with an equimolar amount of sodium allyloxide in allyl alcohol at room temperature. The thermal rearrangement of II was caried out by heating at 150° for 30 minutes, and there were isolated seven kinds of products. Thus, the reaction mixture was dissolved in chloroform, and the chloroform-insoluble part subjected to fractional recrystallization, whereby two kinds of crystals (A and B) were obtained. Since these products showed an acidic property, it was considered that these must be *s*-triazolo[1,5-*a*]pyrimidin-7-ol derivatives. The product (A), m.p. 278~279°, obtained in a very poor yield, was identified with an authentic sample of 5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol[3] (III). The other product (B), m.p. 252~253°, obtained in ca. 50% yield, was in agreement with an isomer of the starting material (II) by the elemental analysis, and its ultraviolet absorption spectrum showed a similar curve to that of III besides the bathochromic shift (8 mμ). This fact suggests that the allyl group migrated to the 6-position of II, on the basis of the discovery*4 that the introduction of alkyl group at 6-position of *s*-triazolo[1,5-*a*]pyrimidine ring produces a bathochromic shift to to the extent of about 7~8 mμ (see Table I). From these results, it was considered that B was the Claisen rearrangement product, 5-methyl-6-allyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (IV). Thus, B was identified with the product (IV) obtained by condensation of ethyl 2-acetyl-4-pentenoate with 5-amino-*s*-triazole in boiling glacial acetic acid.

On the other hand, from the chloroform-soluble part of the thermal rearrangement product, a small amount of an oily substance (C) and four kinds of crystals (D, E, F and G)

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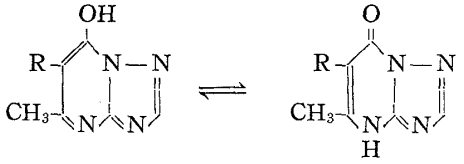
*2 Part XIV. Y. Makisumi : Bulletin, **11**, 845 (1963).

*3 We entitle "alkyl rearrangement" to such thermal rearrangement.

*4 The bathochromic effect due to halogen atom at 6-position of the *s*-triazolo[1,5-*a*]pyrimidine ring was studied in the previous paper. (Y. Makisumi : This Bulletin, **9**, 808 (1961)).

1) Y. Makisumi, H. Kano : This Bulletin, **11**, 67 (1963).
2) D. S. Tarbell : Org. Reactions, **2**, Charp. 1 (1944).
3) C. Bülow, K. Haas : Ber., **42**, 4638 (1909); K. Shirakawa : Yakugaku Zasshi, **78**, 1395 (1958).

TABLE I. Ultraviolet Absorption Spectra of 5-Methyl-6-alkyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ols



No.	R	m.p. (°C)	λ_{max}^{EtOH} mμ (log ε)			$\Delta\lambda^{d)}$ (mμ)
III	H	278~279	240 (3.62)	272	(4.02)	
IV	CH_2=$CHCH_2$	252~253	247 (3.74)	279	(4.02)	+7
	CH_3	302~303[a)]	247 (3.67)	279	(4.05)	+7
VI	C_2H_5	278~279[b)]	247 (3.73)	279.5	(4.05)	+7.5
VII	C_3H_7	231~232	247 (3.73)	279.5	(4.05)	+7.5
	C_4H_9	227~228.5[c)]	247 (3·72)	279.5	(4.04)	+7.5
	iso-C_4H_9	268~269[c)]	247 (3.74)	280	(4.02)	+8

a) C. F. H. Allen, *et al.*: J. Org. Chem., **24**, 793 (1959).
b) Bülow[5)] gives 268°.
c) Part XVI. Y. Makisumi: This Bulletin **11**, 858 (1963).
d) This means the shifts of the absorption band in the longer wave-length region in comparison with those of III.

were obtained by alumina chromatography, the yields of the latter four crystals being 1.0, 3.5, 2.6 and 11.4%, respectively. C exhibited an absorption band of the nitrile group in its infrared absorption spectrum. Therefore, C seemed to be a substance produced by the decomposition of the *s*-triazolo[1,5-*a*]pyrimidine ring, but the further investigation has not been done yet. Among the crystalline products, E, m.p. 143.5~144.5°, and G, m.p. 195~196°, gave the analytical values which were in agreement with that of the starting material (II) and the other products (D), m.p. 110~111°, and (F), m.p. 180~181°, showed the analytical values corresponding to $C_{12}H_{14}ON_4$ which is identical with the one resulting from the introduction of an allyl group into III. These compounds (D, E, F, and G) were neutral, and exhibited an absorption band of the carbonyl group in each infrared absorption spectrum. These facts suggest that they must be N-allyl-*s*-triazolo[1,5-*a*]pyrimidine-7-one derivatives produced by the migration of the allyl group to the ring nitrogen. Furthermore, in the ultraviolet absorption spectrum, E exhibited absorption bands at 246 and 276.5 mμ corresponding to those[1)] of 4-alkyl-5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-ones and G did absorption bands at 247.5 and 284 mμ corresponding to those[1)] of 3-alkyl-5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-ones. From these results, E and G were assigned to 4-allyl-5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (IIIa) and 3-allyl-5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-one (IIIb), respectively. The respective absorption bands of D and F were also exhibited at 248, 285, 252.5 and 291.5 mμ, those in the longer wave-length region showing the bathochromic shift to the extent of 7.5~8.5 mμ in comparison with those of E and G, in their ultraviolet absorption spectra. This bathochromic shift suggests that D and F must be identical with the compounds resulting from the introduction of an allyl group into the 6-position of E and G. Accordingly, D and F were also assigned to 5-methyl-4,6-diallyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (IVa) and 5-methyl-3,6-diallyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-one (IVb), respectively. It was completely established by the following experiments that these N-allyl products had the expected structure.

In order to synthesize independently the above 3- and 4-allyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H* and 4*H*)-one derivatives, two kinds of N-allyl derivatives of 5-amino-*s*-triazole as intermediates were prepared. S-Methylisothiosemicarbazide iodide was converted into 1-allyl-2-aminoguanidinium sulfate by the action of allylamine and the following treatment with silver sulfate. The resulting sulfate was heated with formic

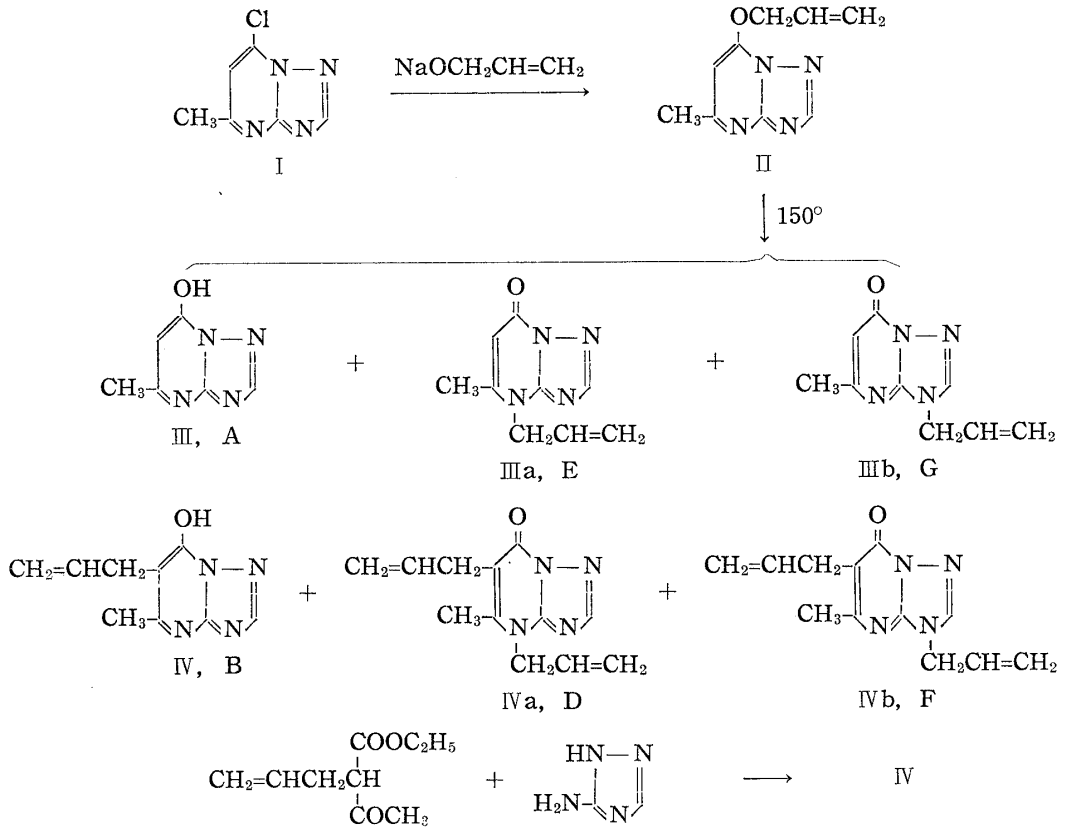


Chart 1.

acid to give 1-allyl-2-formylaminoguanidinium sulfate, which was converted into two kinds of N-allyl-5-amino-*s*-triazoles by the action of sodium carbonate. The minor product (Va) of m.p. 117° which was easily soluble in hot benzene, was decided to be 5-allylamino-*s*-triazole and the major product (Vb) of m.p. 157~158° which was difficultly soluble in hot benzene, to be 3-amino-4-allyl-4*H*-*s*-triazole from the results of elemental analysis and diazo-coupling test towards the aromatic primary amines.

Condensation of ethyl acetoacetate with Va by heating at 200° without solvent afforded 4-allyl-7-methyl-*s*-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one (IIIc) of m.p. 118~119° as the major product and IIIa of m.p. 143.5~144.5° as the minor product. However, using glacial acetic acid as the solvent, there were obtained IIIa as the major product and IIIc as the minor product. On the other hand, condensation of ethyl acetoacetate with Vb while heating without solvent gave IIIb of m.p. 195~196° and 3-allyl-7-methyl-*s*-triazolo[1,5-*a*]-pyrimidin-5(3*H*)-one (IIId) of m.p. 170~171° in compatible yields. But, when glacial acetic acid was employed as the solvent in this reaction, only IIIb was obtained. The structure of these condensates (IIIa~IIId) was determined on the basis of the elemental analysis and the infrared and ultraviolet absorption spectra. Namely, the elemental analysis of these products (IIIa, IIIb, IIIc and IIId) were in agreement with the calculated values for $C_9H_{10}ON_4$ and their infrared absorption spectra exhibited an absorption band of the carbonyl group at 1703, 1686, 1677 and 1649 cm^{-1}, respectively. IIIa and IIIb showed an absorption curve corresponding to that of the *s*-triazolo[1,5-*a*]pyrimidin-7-(3*H* or 4*H*)-one derivative and IIIc and IIId showed an absorption curve corresponding to that of the *s*-triazolo[1,5-*a*]pyrimidin-5(3*H* or 4*H*)-one derivative in the ultraviolet absorption spectrum. Moreover, it was confirmed by admixture and the infrared and ultraviolet absorption spectra comparison that IIIa and IIIb were respectively identical with E and G obtained by the thermal rearrangement of II.

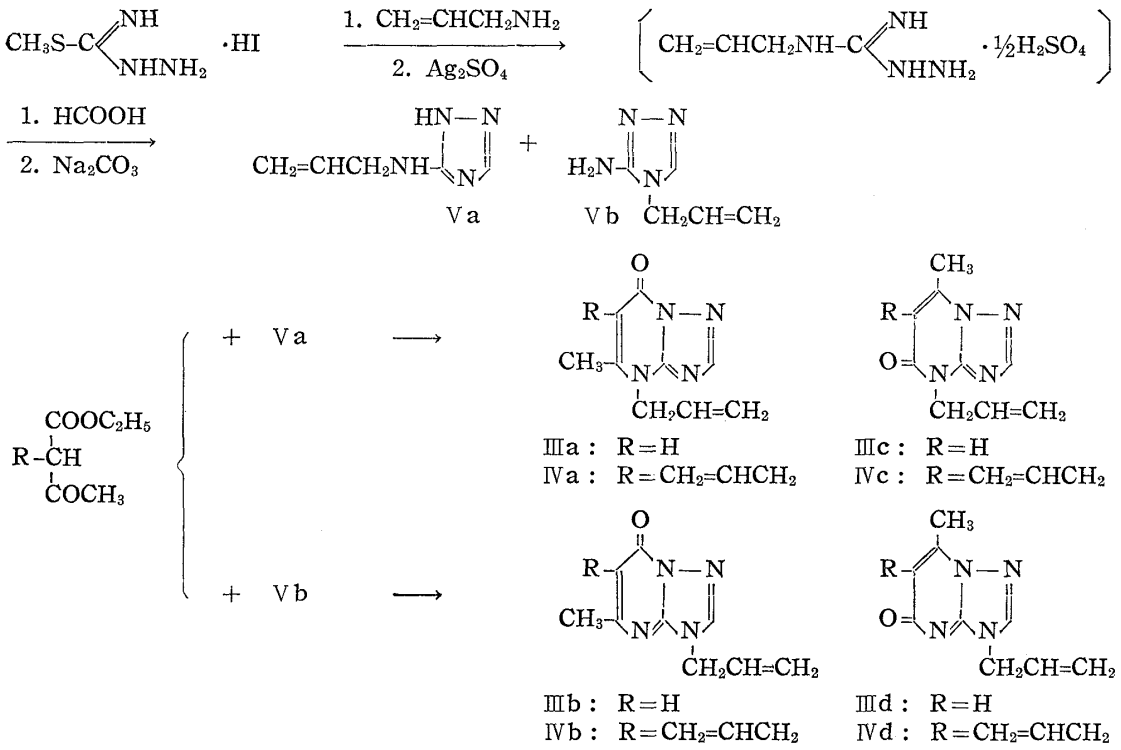


Chart 2.

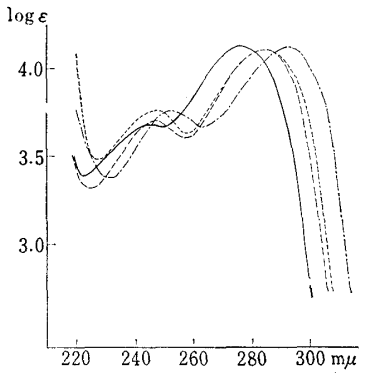


Fig. 1. Ultraviolet Absorption Spectra (in EtOH)

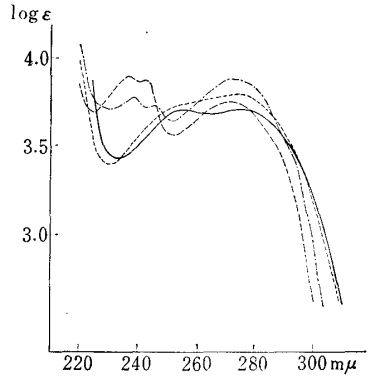
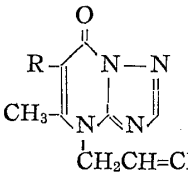
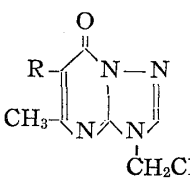


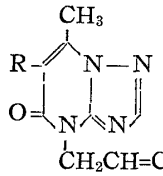
Fig. 2. Ultraviolet Absorption Spectra (in EtOH)



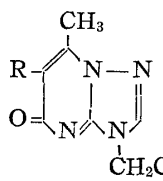
——— IIIa : R=H
---------- IVa : R=CH2=CHCH2



– – – – IIIb : R=H
—·—·— IVb : R=CH2=CHCH2



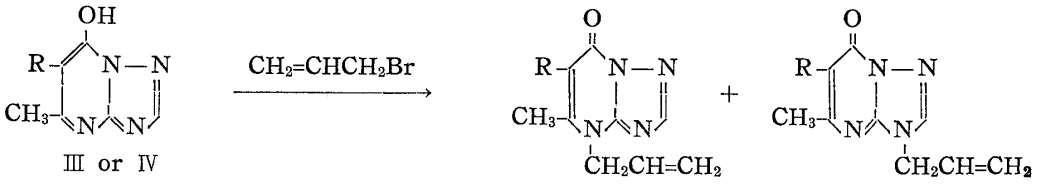
——— IIIc : R=H
---------- IVc : R=CH2=CHCH2



– – – – IIId : R=H
—·—·— IVd : R=CH2=CHCH2

Similarly, condensation of ethyl 2-acetyl-4-pentenoate with Va by heating without solvent or with glacial acetic acid afforded IVa of m.p. 110.5~111° and 7-methyl-4,6-diallyl-*s*-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one (IVc) of m.p. 54.5~55°. In these reaction, IVc was obtained predominantly in the case without solvent, while IVa yielded predominantly in the case of using glacial acetic acid. Condensation of ethyl 2-acetyl-4-pentenoate with Vb while heating without solvent gave IVb of m.p. 180~181° and 7-methyl-3,6-diallyl-*s*-triazolo[1,5-*a*]pyrimidin-5(3*H*)-one (IVd) of m.p. 158.5~159.5° in compatible yields. But, when glacial acetic acid was used as the solvent in this reaction, only IVb was obtained. The structure of these condensates (IVa~IVd) was also determined by the results of the elemental analysis and the infrared and ultraviolet absorption spectra as well as the above experimental results. Furthermore, IVa and IVb were respectively identical with D and F obtained by the thermal rearrangement of II, by admixture and the infrared and ultraviolet absorption spectra comparison.

In connection with the above thermal rearrangement reaction, allylation of the *s*-triazolo[1,5-*a*]pyrimidin-7-ol derivatives (III and IV) was also investigated. Reaction of III with allyl bromide in the presence of potassium hydroxide in aqueous ethanol resulted in formation of the two allylated products which were respectively identical with the 4- and 3-allyl compounds (IIIa and IIIb) obtained by the thermal rearrangement of II. Similarly, allylation of IV in the same mannor afforded the two allylated products which were respectively identical with the 4- and 3-allyl compounds (IVa and IVb) obtained by the same thermal rearrangement reaction. These results were consistent with that of the alkylation of III in the previous work.[4]

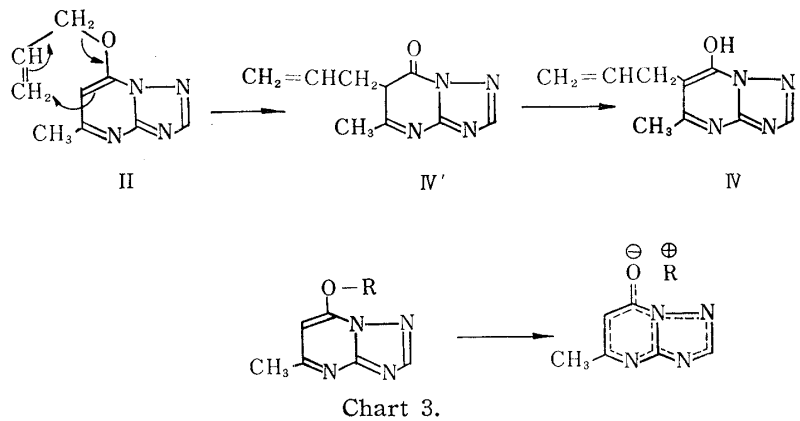


III or IV　　IIIa or IVa　　IIIb or IVb

The mechanism of this rearrangement described above are considered as follows :

(1) It has been well-known that the *ortho*-Claisen rearrangement is the intramolecular rearrangement[2] involving a six-membered ring transition state. Accordingly, it is evident that the 6-allyl derivative (IV) is produced by the intramolecular rearrangement as shown in Chart 3.

(2) All the products obtained by this rearrangement reaction are stable for heating and not transformed to each other.



II　　IV'　　IV

Chart 3.

4) Y. Makisumi : This Bulletin **11**, 129 (1963).

(3) The diallyl derivatives (IVa and IVb) are obtained in this reaction.

From these facts, it is concluded that the migration of the allyl group to the ring nitrogens at the 3- and 4-positions is the intermolecular rearrangement which occurs independently with the *ortho*-Claisen rearrangement. Therefore, it may be deduced that the alkyl rearrangement of the 7-alkoxy-*s*-triazolo[1,5-*a*]pyrimidine derivatives is an intermolecular reaction. It is considered that this rearrangement proceeds by a mechanism involving ion-pair collapse and intermolecular alkylation.

Experimental[*5]

5-Methyl-7-allyloxy-*s*-triazolo[1,5-*a*]pyrimidine (II)——To a solution of 0.85 g. of Na in 120 cc. of allyl alcohol, 6.3 g. of 5-methyl-7-chloro-*s*-triazolo[1,5-*a*]pyrimidine (I) was added in small portions under stirring and cooling. The mixture was stirred for 3 hr. at room temperature and the precipitated NaCl was filtered off. The filtrate was concentrated to dryness under reduced pressure, the residue was diluted with H_2O, and extracted with $CHCl_3$. The extract was washed with H_2O and dried over $MgSO_4$. After removal of the solvent, the residue (6.3 g.) was dissolved in benzene and purified by alumina chromatography giving colorless needles, m.p. 108~109°. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30; N, 29.46. Found : C, 56.95; H, 5.46; N, 29.18.

Thermal Rearrangement of II——Five grams of II was heated at 150° for 30 min., by which the crystals were liquefied and solidified immediately. After cool, the solid was dissolved in $CHCl_3$ and 2.65 g. of the $CHCl_3$-insoluble crystals, m.p. 246~248° were collected by filtration. These crystals were separated to 20 mg. of colorless pillars (A), m.p. 278~279° and 2.55 g. of colorless needles (B), m.p. 252~253° by fractional recrystallization. A was identified with an authentic sample of 5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (III). B was shown to be identical with 5-methyl-6-allyl-*s*-triazolo[1,5-*a*]-pyrimidin-7-ol (IV) by mixed melting point and comparison of their IR and UV spectra. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30; N, 29.46. Found. C, 56.78; H, 5.53; N, 29.38.

The $CHCl_3$-soluble part of this reaction was dissolved in benzene-$CHCl_3$, passed through a column of alumina, and eluted with benzene-$CHCl_3$, $CHCl_3$ and $CHCl_3$-EtOH. The first fraction obtained from benzene-$CHCl_3$ (3:1) eluate gave 30 mg. of an oily substance (C), which was not characterized. The second fraction obtained from the same solvents eluate gave 50 mg. of colorless pillars (D), m.p. 110~111°, on recrystallization from petr. benzin. This compound was identified with 4,6-diallyl-5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (IVa) by mixed melting point and comparison of their IR and UV spectra. *Anal.* Calcd. for $C_{12}H_{14}ON_4$: C, 62.59; H, 6.13; N, 24.33. Found : C, 62.39; H, 6.35; N, 24.35. The third fraction obtained from the same solvents eluate gave 175 mg. of colorless scales (E), m.p. 143.5~144.5°, on recrystallization from petr. benzin. E was identified with 4-allyl-5-methyl-*s*-triazolo-[1,5-*a*]pyrimidin-7(4*H*)-one (IIIa) by mixed melting point and comparison of their IR and UV spectra. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30; N, 29.46. Found : C, 56.97; H, 5.55; N, 29.53. The next fraction obtaining from $CHCl_3$ eluate afforded 132 mg. of colorless pillars (F), m.p. 180~181°, on recrystallization from benzene. F was identified with 5-methyl-3,6-diallyl-*s*-triazolo[1,5-*a*]pyrimidin-7-(3*H*)-one (IVb) by mixed melting point and comparison of their IR and UV spectra. *Anal.* Calcd. for $C_{12}H_{14}ON_4$: C, 62.59; H, 6.13; N, 24.33. Found : C, 62.71; H, 6.25; N, 24.25. The last fraction eluted with $CHCl_3$-EtOH, afforded 570 mg. of colorless plates (G), m.p. 195~196°, on recrystallization from benzene-EtOH. G was identified with 3-allyl-5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-one (IIIb) by mixed melting point and comparison of their IR and UV spectra. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30; N, 29.46. Found : C, 56.92; H, 5.42; N, 29.36.

5-Methyl-6-allyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (IV)——A mixture of 17 g. of ethyl 2-acetyl-4-pentenoate and 8.4 g. of 5-amino-*s*-triazole in 40 cc. of AcOH was refluxed for 3 hr. After cool, the resulting crystals were collected by filtration, washed with EtOH, and dried giving 11.5 g. of white crystals. Recrystallization from EtOH gave colorless needles, m.p. 252~253°. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30; N, 29.46. Found : C, 56.95; H, 5.42; N, 29.57. IR : $\nu_{C=O}^{Nujol}$ 1692 cm^{-1} (lactam C=O). UV : see Table I.

Synthesis of 5-Allylamino-*s*-triazole (Va) and 3-Amino-4-allyl-4*H*-*s*-triazole (Vb)——To a solution of 46.6 g. of S-methylisothiosemicarbazide·HI in 120 cc. of H_2O, 12.5 g. of allylamine was added and the solution was refluxed for 2 hr., by which CH_3SH evolved vigorously. After removal of the solvent under reduced pressure, 47.6 g. of crude 1-allyl-2-aminoguanidine·HI was obtained. This product was dissolved in 400 cc. of H_2O, acidified with few drops of AcOH, and 31 g. of Ag_2SO_4 was added in small

[*5] All melting points are uncorrected. Infrared spectra were measured with the Kōken Infrared Spectrophotometer, Model DS-301, and ultraviolet spectra were taken with the Hitachi Recording Spectrophotometer, EPS-2.

portions to the solution under vigorous stirring. After the stirring was continued for 2 hr., the precipitated AgI was filtered off and the filtrate was concentrated to dryness under reduced pressure. The residue was dissolved in abs. EtOH, the insoluble inorganic compound was filtered off, and the filtrate was evaporated to give 28.5 g. of crude 1-allyl-2-aminoguanidinium sulfate. This sulfate was formylated with 8.8 g. of HCOOH by heating on a steam bath for 18 hr., the resulting syrup was dissolved in 35 cc. of H_2O, and treated with 8.8 g. of Na_2CO_3 at 50°. The solution was then placed in an evaparating dish, evaporated to dryness on a steam bath, and dried completely over P_2O_5 in a desiccator. This residue was extracted with hot benzene (100 cc. × 4) and further with abs. EtOH (100 cc.) under reflux. The benzene extract was purified by alumina chromatography using Me_2CO as eluent and the first fraction was recrystallized from benzene to give 0.55 g. of 5-allylamino-*s*-triazole (Va) as colorless scales, m.p. 117°. *Anal.* Calcd. for $C_5H_8N_4$: C, 48.37; H, 6.50; N, 45.13. Found : C, 48.58; H, 6.66; N, 44.82. This compound gave a negative diazo-coupling test. The second fraction and the product obtained from the EtOH-extract, were combined and recrystallized from EtOH to give 8.98 g. of 3-amino-4-allyl-4*H*-*s*-triazole (Vb) as colorless pillars, m.p. 157~158°. *Anal.* Calcd. for $C_5H_8N_4$: C, 48.37; H, 6.50; N, 45.13. Found : C, 48.47; H, 6.75; N, 44.95. This compound gave a positive diazo-coupling test.

Condensation of Va with Ethyl Acetoacetate——a) A mixture of 0.1 g. of Va and 0.12 g. of ethyl acetoacetate in 1 cc. of AcOH was refluxed for 6 hr. After removal of the solvent, the residue was dissolved in benzene-$CHCl_3$, passed through a column of alumina, and eluted with benzene-$CHCl_3$ (1:1) and $CHCl_3$. The product obtained from benzene-$CHCl_3$ eluate, was recrystallized from petr. benzin to give 5 mg. of 4-allyl-7-methyl-*s*-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one (IIIc) as colorless pillars, m.p. 118~119°. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.38; H, 5.30; N, 29.46. Found : C, 57.10; H, 5.50; N, 29.20. IR : $\nu_{C=O}^{Nujol}$ 1677 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) : 250.5 (3.71), 271 (3.72).

The product obtained from $CHCl_3$ eluate, was recrystallized from benzene to 90 mg. of 4-allyl-5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (IIIa) as colorless scales, m.p. 143.5~144.5°. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30; N, 29.46. Found : C, 56.95; H, 5.35; N, 29.32. IR : $\nu_{C=O}^{Nujol}$ 1703 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) : 246 (3.69), 276.5 (4.12).

b) A mixture of 0.15 g. of Va and 0.21 g. of ethyl acetoacetate was heated at 180° for 30 min. and then at 200° for 1 hr. After cool, the resulting solids were dissolved in benzene-$CHCl_3$ and purified by alumina chromatography as above. As the major product, 135 mg. of colorless pillars (IIIc), m.p. 118~119° were obtained and as the minor product, 8 mg. of colorless scales (IIIa), m.p. 143.5~144.5° were obtained.

Condensation of Vb with Ethyl Acetoacetate——a) A mixture of 0.5 g. of Vb and 0.62 g. of ethyl acetoacetate in 3 cc. of AcOH was refluxed for 6 hr. After removal of the solvent under reduced pressure, the residue was dissolved in $CHCl_3$-and purified by alumina chromatography. The resulting crystals were recrystallized from benzene-EtOH to give 0.47 g. of 3-allyl-5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-one (IIIb) as colorless plates, m.p. 195~196°. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30; N, 29.46. Found : C, 56.79; H, 5.28; N, 29.51. IR : $\nu_{C=O}^{Nujol}$ 1686 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) : 247.5 (3.70), 284 (4.10).

b) A mixture of 0.9 g. of Vb and 1.4 g. of ethyl acetoacetate was heated at 180° for 30 min. and then at 200° for 30 min. After cool, the resulting solid was dissolved in $CHCl_3$, passed through a column of alumina, and eluted with $CHCl_3$ affording two fractions. The first fraction gave 0.13 g. of colorless plates (IIIb), m.p. 195~196°, on recrystallization from benzene-EtOH. The second fraction gave 0.205 g. of 3-allyl-7-methyl-*s*-triazolo[1,5-*a*]pyrimidin-5(3*H*)-one (IIId) as colorless plates, m.p. 170~171°, on recrystallization from benzene. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30; N, 29.46. Found : C, 57.08; H, 5.58; N, 29.61. IR : $\nu_{C=O}^{Nujol}$ 1649 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) : 236.5 (3.91), 243 (3.89), 270 (3.75).

Condensation of Va with Ethyl 2-Acetyl-4-pentenoate——a) A mixture of 0.1 g. of Va and 0.17 g. of ethyl 2-acetyl-4-pentenoate in 1 cc. of AcOH was refluxed for 5 hr. and the solvent was removed under reduced pressure. The residue was dissolved in benzene-$CHCl_3$, passed through a column of alumina, and eluted with benzene-$CHCl_3$ (1:1) affording the two fractions. The first fraction gave 7 mg. of 7-methyl-4,6-diallyl-*s*-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one (IVc) as colorless pillars, m.p. 54.5~55.5°, on recrystallization from petr. benzin. *Anal.* Calcd. for $C_{12}H_{14}ON_4$: C, 62.59; H, 6.13; N, 24.33. Found : C, 62.37; H, 6.29; N, 24.23. IR : $\nu_{C=O}^{Nujol}$ 1668 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) : 255 (3.77), 273.5 (3.83). The second fraction gave 195 mg. of 5-methyl-4,6-diallyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (IVa) as colorless pillars m.p. 110~111°, on recrystallization from petr. benzin. *Anal.* Calcd. for $C_{12}H_{14}ON_4$: C, 62.59; H, 6.13; N, 24.33. Found: C, 62.68; H, 6.28; N, 24.15. IR: $\nu_{C=O}^{Nujol}$ 1686 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε): 248 (3.77), 285 (4.10).

b) A mixture of 0.15 g. of Va and 0.27 g. of ethyl 2-acetyl-4-pentenoate was heated at 180° for 30 min. and then at 200° for 1 hr. and the reaction mixture was purified by alumina chromatography as above. The first fraction gave 130 mg. of colorless pillars (IVc), m.p. 54.5~55°(from petr. benzin) and the second fraction gave 5 mg. of colorless pillars (IVa), m.p. 110~111°(from petr. benzin).

Condensation of Vb with Ethyl 2-Acetyl-4-pentenoate——a) A mixture of 0.5 g. of Vb and 0.8 g. of ethyl 2-acetyl-4-pentenoate in 3 cc. of AcOH was refluxed for 6 hr. After removal of the solvent

under reduced pressure, the residue was dissolved in $CHCl_3$ and purified by chromatography through an alumina column. The resulting crystals were recrystallized from benzene to give 0.32 g. of 5-methyl-3,6-diallyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-one (IVb) as colorless pillars, m.p. 180~181°. *Anal.* Calcd. for $C_{12}H_{14}ON_4$: C, 62.59; H, 6.13; N, 24.33. Found: C, 62.71; H, 6.36; N, 24.19. IR: $\nu_{C=O}^{Nujol}$ 1669 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε): 252.5 (3.78), 291.5 (4.12).

b) A mixture of 0.45 g. of Vb and 0.92 g. of ethyl 2-acetyl-4-pentenoate was heated at 180° for 30 min. and then at 200° for 20 min. The reaction mixture was dissolved in $CHCl_3$, passed through a column of alumina, and eluted with $CHCl_3$ affording the two fractions. The first fraction gave 70 mg. of colorless pillars (IVb), m.p. 180~181°, on recrystallization from benzene. The second fraction gave 90 mg. of 7-methyl-3,6-diallyl-*s*-triazolo[1,5-*a*]pyrimidin-5(3*H*)-one (IVd) as colorless plates, m.p. 158.5~159.5°, on recrystallization from benzene. *Anal.* Calcd. for $C_{12}H_{14}ON_4$: C, 62.59; H, 6.13; N, 24.33. Found: C, 62.84; H, 6.32; N, 24.36. IR: $\nu_{C=O}^{Nujol}$ 1650 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε): 238.5 (3.78), 245 (3.73), 272 (3.87).

Allylation of III with Allyl Bromide——To a solution of 5 g. of KOH in 100 cc. of 85% EtOH, 6 g. of finely powdered III and then 9 g. of allyl bromide were added and the mixture was heated under gentle reflux for 2.5 hr. After removal of the solvent under reduced pressure, the residue was dried over P_2O_5 in a desiccator and then extracted with $CHCl_3$ (50 cc. × 2) under reflux. The insoluble crystals were dissolved in H_2O and acidified with 10% HCl to give 0.68 g. of III. The $CHCl_3$-extract was concentrated to dryness and the residue was dissolved in benzene-$CHCl_3$ (2:1). This solution was passed through a column of alumina and eluted with benzene-$CHCl_3$ and $CHCl_3$. The crystals obtained from benzene-$CHCl_3$ eluate, were recrystallized from benzene to give 1.73 g. of colorless scales, m.p. 143.5~144.5°, which were identified with IIIa by melting point determination on admixture and IR spectrum comparison. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30; N, 29.46. Found: C, 56.79; H, 5.35; N, 29.31. The crystals obtained from $CHCl_3$ eluate, were recrystallized from benzene-EtOH to give 1.87 g. of colorless plates, m.p. 195~196°, which were identified with IIIb by the mixed melting point determination and by comparison of IR spectra. *Anal.* Calcd. for $C_9H_{10}ON_4$: C, 56.83; H, 5.30, N, 29.46. Found: C. 56.89; H, 5.42; N, 29.35.

Allylation of IV with Allyl Bromide——To a solution of 2.5 g. of KOH in 85% EtOH, 3.8 g. of IV and then 4.5 g. of allyl bromide were added and the solution was heated under gentle reflux for 2.5 hr. After removal of the solvent, the residue was treated as above. IV (0.58 g.) was recovered from the $CHCl_3$-insoluble crystals. The $CHCl_3$-soluble part was separated to the two fractions by alumina chromatography. The first fraction gave 1.45 g. of colorless pillars, m.p. 110~111°, on recrystallization from petr. benzin. This compound was identified with IVa by admixture and IR spectral comparison. *Anal.* Calcd. for $C_{12}H_{14}ON_4$: C, 62.59; H, 6.13; N, 24.33. Found: C, 62.41; H, 6.33; N, 24.20. The second fraction gave 1.68 g. of colorless pillars, m.p. 180~181°, on recrystallization from benzene. This compound was also identified with IVb by admixture and IR spectral comparison. *Anal.* Calcd. for $C_{12}H_{14}ON_4$: C, 62.59; H, 6.13; N, 24.33. Found: C, 62.60; H, 6.24; N, 24.29.

5-Methyl-6-ethyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (VI)——This compound was prepared by the method of Bülow and Haas[5] from ethyl 2-ethylacetoacetate and 5-amino-*s*-triazole. Recrystallization from EtOH gave colorless pillars, m.p. 278~279°. *Anal.* Calcd. for $C_8H_{10}ON_4$: C, 53.92; H, 5.66; N, 31.45. Found: C, 53.95; H, 5.76; N, 31.32. UV: see Table I.

5-Methyl-6-propyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (VII)——a) A mixture of 17.2 g. of ethyl 2-acetylvaleroate and 8.4 g. of 5-amino-*s*-triazole in 36 cc. of AcOH was heated under reflux for 6 hr. After cool, the precipitated crystals were collected by filtration and recrystallized from 60% EtOH to give 12.4 g. of colorless pillars, m.p. 230~231°. *Anal.* Calcd. for $C_9H_{12}ON_4$: C, 56.23; H, 6.29; N, 29.15. Found: C, 56.35; H, 6.46; N, 29.21. UV: see Table I.

b) A solution of 0.8 g. of IV in 100 cc. of 50% EtOH was shaken in H_2 at ordinary pressure over 0.2 g. of 5% Pd-C and one mole of H_2 was absorbed during 20 min. After removal of the catalyst, the solvent was evaporated to dryness under reduced pressure. The residue was recrystallized from 60% EtOH to give 0.71 g. of colorless pillars, m.p. 230~231°, which showed no depression of melting point on admixture with VII obtained by method a).

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Summasy

Thermal rearrangement of 5-methyl-7-allyloxy-*s*-triazolo[1,5-*a*]pyrimidine (II) was investigated and seven kinds of products; an unknown oil, 5-methyl-*s*-triazolo[1,5-*a*]-pyrimidin-7-ol (III), its 6-allyl derivative (IV), 3- and 4-allyl-5-methyl-*s*-triazolo[1,5-*a*]-pyrimidin-7(3*H* and 4*H*)-ones (IIIb and IIIa), and their 6-allyl derivatives (IVb and IVa) were obtained. In order to confirm the structure of these products, the condensation of ethyl acetoacetate or its 2-allyl compound with N-allyl derivatives (Va and Vb) of 5-amino-*s*-triazole was examined. On the other hand, allylation of III and IV afforded the 3- and 4-allylated products which were respectively identified with the compounds (IIIa, IIIb and IVa, IVb) obtaining by the thermal rearrangement of II. The mechanism of the above thermal rearrangement reaction was discussed.

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148. Yasuo Makisumi : Studies on Azaindolizine Compounds. XVI.*2 The Allyl Rearrangement of 7-Allyloxy-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidime.

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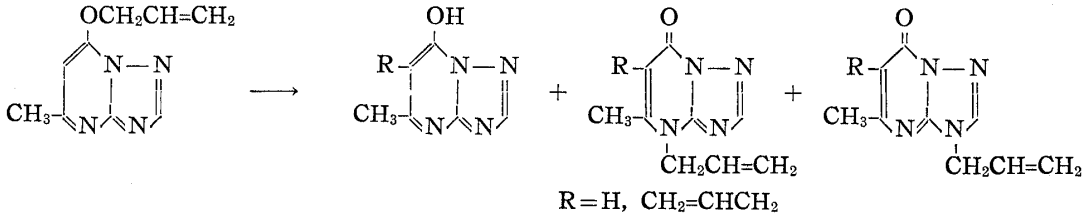
In the foregoing paper*2 of this series, it was disclosed that the *ortho*-Claisen rearrangement occurs as the major reaction and the alkyl rearrangement*3 attends as the minor reaction on heating 5-methyl-7-allyloxy-*s*-triazolo[1,5-*a*]pyrimidine. Moreover, it was confirmed that the alkyl rearrangement is the intermolecular reaction.



It has been well-known that aromatic allylic ethers possessing substituents at both *ortho*-positions, undergo the *para*-Claisen rearrangement[1] on heating.

In the present paper, the thermal rearrangement of 7-allyloxy-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidine (III) possessing a substituent at the *ortho*-position of the allyloxyl group, was investigated.

The starting material (III) was synthesized by the reaction of 7-chloro-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidine (II) with an equimolar amount of sodium allyloxide in allyl alcohol at room temperature. II was prepared from 5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol[2] (I) by the action of phosphoryl chloride. III was an oily substance, which

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*1 Fukushima-ku, Osaka (牧角徳夫).
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*3 This indicates the migration of the allyl group to the ring nitrogens at the 3- and 4-positions.
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