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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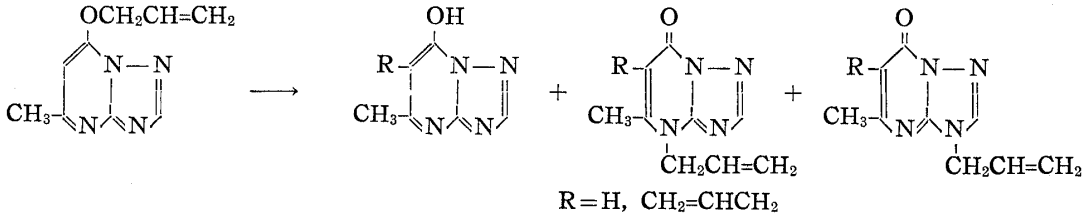
In the foregoing paper*2 of this series, it was disclosed that the *ortho*-Claisen rearrangement occurs as the major reaction and the alkyl rearrangement*3 attends as the minor reaction on heating 5-methyl-7-allyloxy-*s*-triazolo[1,5-*a*]pyrimidine. Moreover, it was confirmed that the alkyl rearrangement 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).
*2 Part XV. Y. Makisumi : This Bulletin, **11**, 851 (1963).
*3 This indicates the migration of the allyl group to the ring nitrogens at the 3- and 4-positions.
1) D. S. Tarbell : Org. Reactions, **2**, Charp. 1 (1944).
2) C. F. H. Allen, *et al.* : J. Org. Chem.. **24**, 793 (1959).

could not be purified by distillation *in vacuo*, because of the transformation to several compounds on heating as described below. So, III was purified by alumina chromatography.

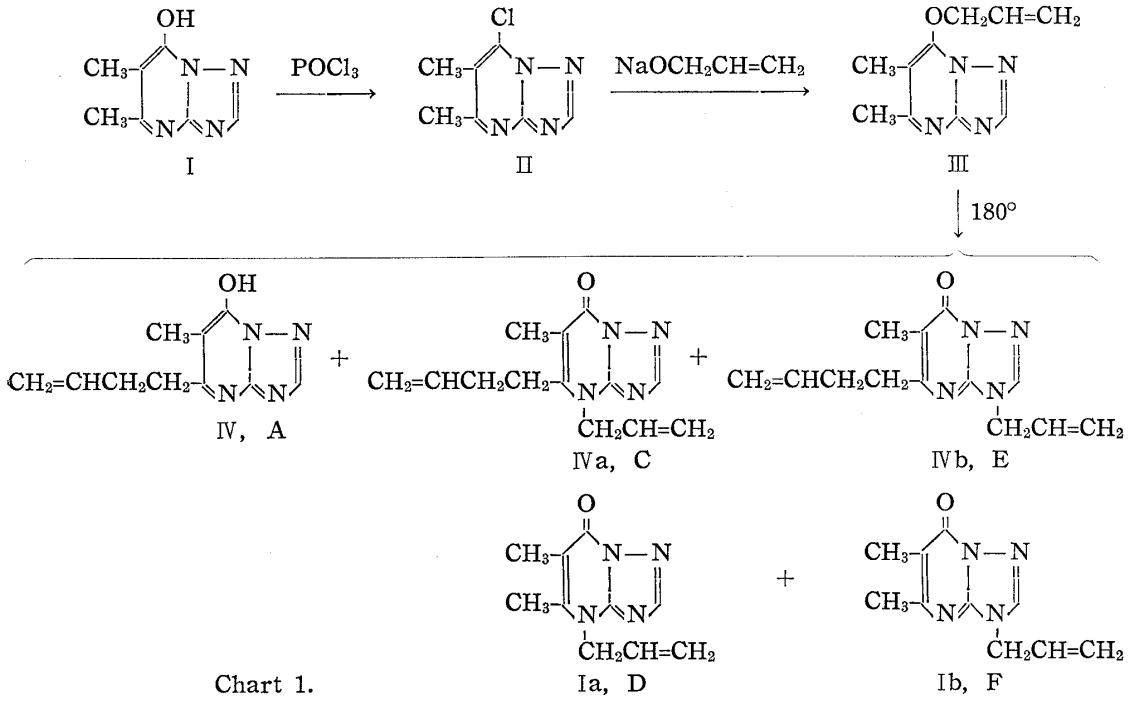


Chart 1.

When III was heated at 180° for one hour without solvent, six kinds of products were isolated. The reaction mixture was dissolved in chloroform, and there was obtained the product (A) of m.p. 241~242° as insoluble crystals in ca. 66% yield. This compound was an acidic substance corresponding to an isomer of the starting material and showed a similar curve to that of I in the ultraviolet absorption spectrum. Consequently, it was considered that A had the structure resulting from the migration of the allyl group in III to one of the methyl groups at the 5- and 6-positions. A was converted into the corresponding 7-chloro derivative (V) by the action of phosphoryl chloride. Since A was difficultly soluble in the usual solvent, the nuclear magnetic resonance spectrum of V was observed and compared with that of II. The spectrum of II showed the three signal peaks at 1.54, 7.27 and 7.49 τ, and these signals were assigned to a ring proton at C_2, methyl protons at C_5, and methyl protons at C_6, respectively from the results of the previous nuclear magnetic resonance study[3] of the *s*-triazolo[1,5-*a*]pyrimidine derivatives. In the spectrum of V, although the signal peaks of a ring proton at C_2 and methyl protons at C_6 appeared at 1.54 and 7.49 τ respectively, that of methyl protons at C_5 disappeared and the signals of one methine proton and three methylene protons were recognized instead. Accordingly, the structure of V was established to be 5-(3-butenyl)-6-methyl-7-chloro-*s*-triazolo[1,5-*a*]pyrimidine. V was also reversible to A by hydrolysis with aqueous sodium hydroxide. Therefore, the structure of A obtained by the above thermal rearrangement of III was also decided to be 5-(3-butenyl)-6-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (IV). On the other hand, it was confirmed by the following experiments that A was neither VII′ nor VIII′ resulting from the migration of the allyl group to the methyl group at the 6-position. Condensation of 5-amino-*s*-triazole with ethyl 2-acetylhexanoate and ethyl 2-acetyl-4-methylpentanoate in boiling glacial acetic acid afforded 5-methyl-6-butyl- and 5-methyl-6-isobutyl-

3) Y. Makisumi, H. Watanabe, K. Tori : To be published (presented of the Kinki Branch Meeting of the Pharmaceutical Society of Japan, October 20, 1962).

s-triazolo[1,5-*a*]pyrimidin-7-ols (Ⅶ and Ⅷ), respectively. These products were not identified with the compound (Ⅵ) which was obtained by catalytic reduction of A. By this result, it was also supported that the structure of Ⅴ determined by the nuclear magnetic resonance study was correct.

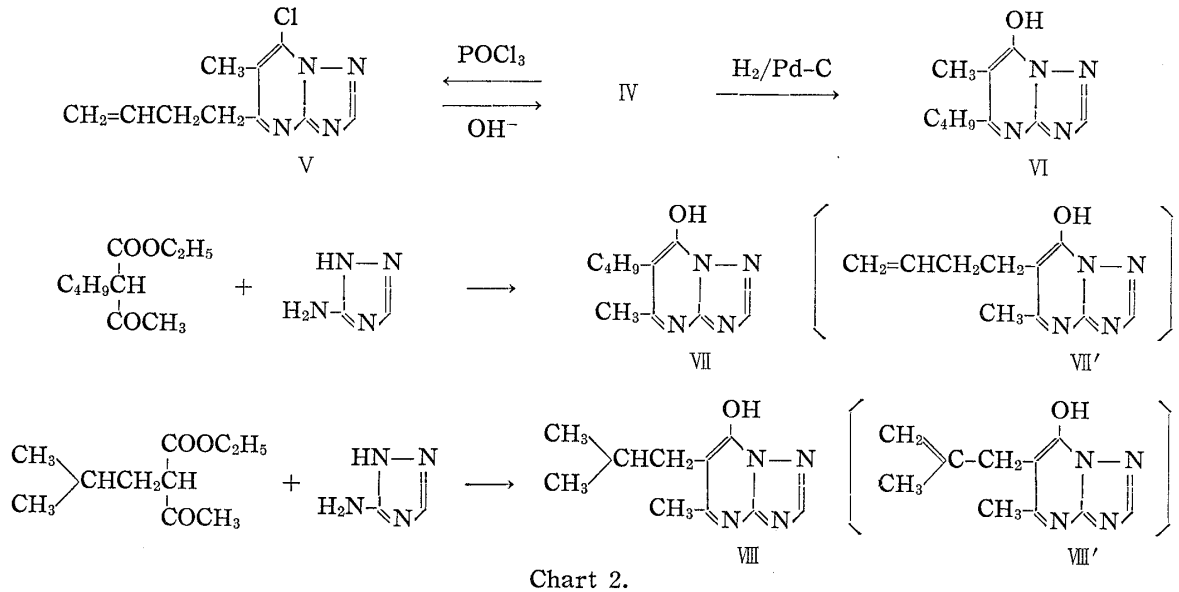


Chart 2.

The chloroform-soluble products in the thermal rearrangement of Ⅲ were separated to a small amount of an oily substance (B) and four kinds of crystals (C, D, E and F) by alumina chromatography, the yields of the latter four crystals being 0.02, 3.24, 0.12 and 5.5%, respectively. B exhibited an absorption band of the nitrile group in the infrared absorption spectrum. Therefore, B was seemed to be a substance which was produced by decomposition of the *s*-triazolo[1,5-*a*]pyrimidine ring, but the further investigation has not been done yet. The elemental analysis of the four crystalline products showed that D, m.p. 170~171°, and F, m.p. 204~205°, were in agreement with the isomers of the starting material (Ⅲ) and the other products (C, m.p. 99~99.5°, and E, m.p. 167~168°), had the formula, $C_{12}H_{14}ON_4$, corresponding to the one resulting from the introduction of an allyl group to Ⅲ. These products (C, D, E and F) were neutral and exhibited an absorption band of the carbonyl group at 1676, 1685, 1674 and 1671 cm^{-1} respectively in their infrared absorption spectra. These facts suggest that these products must be the N-allyl-*s*-triazolo[1,5-*a*]pyrimidin-7-one derivatives which were produced by the migration of the allyl group to the ring nitrogen of the *s*-triazolo-[1,5-*a*]pyrimidine ring. Furthermore, these products respectively showed an absorption curve corresponding to that of 4- or 3-alkyl-*s*-triazolo[1,5-*a*]pyrimidin-7 (4*H* or 3*H*)-one derivatives.*[2,4]

In order to confirm the structure of these products, the synthesis of 3- and 4-allyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H* and 4*H*)-one derivatives was attempted. Condensation of ethyl 2-methylacetoacetate with 5-allylamino-*s*-triazole*[2] by heating without solvent or in glacial acetic acid afforded 4-allyl-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (Ia) of m.p. 170~171° and 4-allyl-6,7-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one (Ic) of m.p. 101~102°. In this reaction, Ic was predominantly obtained in the case without solvent and Ia was predominantly obtained in the case of using glacial acetic acid as the solvent. Condensation of ethyl 2-methylacetoacetate with 3-amino-4-allyl-4*H*-*s*-triazole*[2] by heating without solvent gave 3-allyl-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-

4) Y. Makisumi, H. Kano : This Bulletin, **11**, 67 (1963).

7(3*H*)-one (Ib) of m.p. 204~205° and 3-allyl-6,7-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-5(3*H*)-one (Id) of m.p. 175~175.5° in compatible yields. But, when glacial acetic acid was employed as the solvent in this reaction, there was obtained only Ib. The structure of these condensates (Ia~Id) was determined by elemental analysis and infrared and ultraviolet absorption spectra. Namely, these condensates gave the values corresponding to the formula, $C_{10}H_{12}ON_4$, in the elemental analysis and exhibited absorption bands of the carbonyl group in their infrared absorption spectra. Ia and Ib showed absorption curves corresponding to that[*2,4] of the *s*-triazolo[1,5-*a*]pyrimidin-7(3*H* or 4*H*)-one derivative and Ic and Id also showed absorption curves corresponding to that[*2,4] of the *s*-triazolo[1,5-*a*]pyrimidin-5(3*H* or 4*H*)-one derivative in the ultraviolet absorption

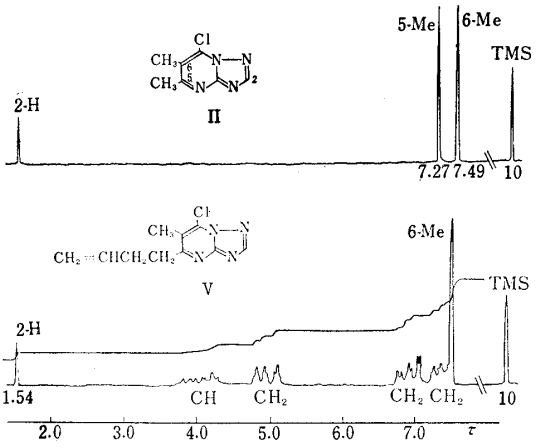


Fig. 1. Nuclear Magnetic Resonance Spectra of 7-Chloro-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidine (II) (top) and 5-(3-Butenyl)-6-methyl-7-chloro-*s*-triazolo[1,5-*a*]-pyrimidine (V) (bottom) in Deuterochloroform at 60 Mc.

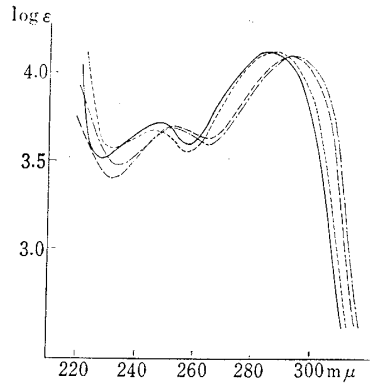


Fig. 2. Ultraviolet Absorption Spectra (in EtOH)

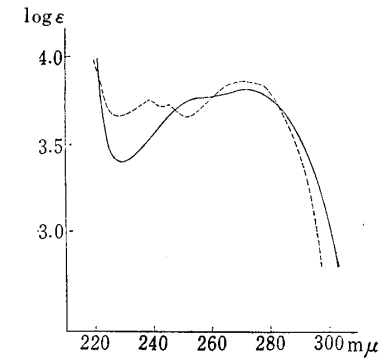
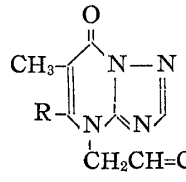
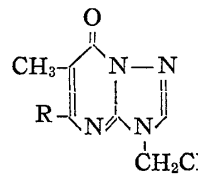


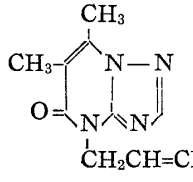
Fig. 3. Ultraviolet Absorption Spectra (in EtOH)



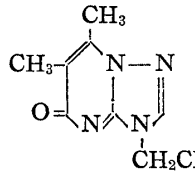
——— Ia : R=CH_3
---------- IVa : R=CH_2=$CHCH_2CH_2$



– – – – Ib : R=CH_3
—·—·— IVb : R=CH_2=$CHCH_2CH_2$



—— Ic



------ Id

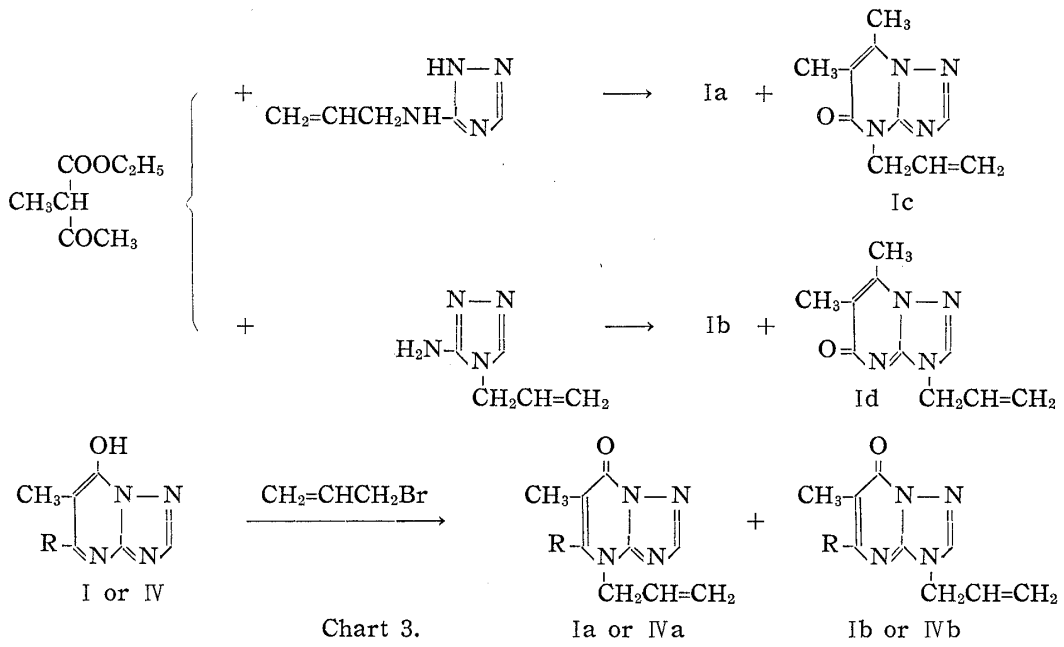


Chart 3.

spectra as shown in Figs. 1 and 2. Moreover, Ia and Ib were respectively identical with D and F obtained by the thermal rearrangement of III, by the mixed melting points and comparison of their infrared and ultraviolet spectra.

In the previous papers,*[2,5] it was reported that the alkylation of the *s*-triazolo[1,5-*a*]-pyrimidin-7-ol derivatives resulted in formation of the corresponding 3- and 4-alkylated derivatives. So, the allylation of I and IV was undertaken. Reaction of I with allyl bromide in the presence of potassium hydroxide in aqueous ethanol afforded the two allylated products which were identical with the 4- and 3-allyl derivatives (Ia and Ib), respectively. Similarly, allylation of IV gave two allylated products, IVa of m.p. 99~99.5° and IVb of m.p. 167~168°. IVa showed a similar curve to that of Ia and IVb showed a similar curve to that of Ib in the ultraviolet absorption spectra as shown in Fig. 1. Consequently, IVa and IVb respectively were deduced to be 4-allyl-5-(3-butenyl)-6-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one and 3-allyl-5-(3-butenyl)-6-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-one. Moreover, IVa and IVb were respectively identical with C and E obtained by the thermal rearrangement of III.

The mechanism of this rearrangement reaction will be discussed. It is evident from the result of the previous work*[2] that the migration of the allyl group to the ring nitrogens at the 3- and 4-positions ("alkyl rearrangement") is an intermolecular rearrangement. As all the products obtained by the thermal rearrangement of III are stable for heating and not transformed to each other, it is considered that the migration of the allyl group to the methyl group at the 5-position is an independent reaction from the alkyl rearrangement. Recently, "out-of-ring" migration[6] of an allyl group to the β-carbon of an *ortho*- or *para*-propenyl side chain was reported and this out-of-ring migration was considered to proceed by two or three consecutive "cycles" in view of the fact[7] that the *para*-Claisen rearrangement involves two successive cyclic stages,

5) Y. Makisumi: This Bulletin, **11**, 129 (1963).
6) W.M. Lauer, D.W.Wujciak: J. Am. Chem. Soc., **78**, 5601 (1956); K. Schmid, P. Fahrini, H. Schmid: Helv. Chim. Acta, **39**, 708 (1956); A. Nickon, B.R. Aaronoff: J. Org. Chem., **27**, 3379 (1962).
7) C.D. Hurd, M.A. Pollack: J. Org. Chem., **3**, 550 (1939); K. Schmid, W. Haegele, H. Schmid: Helv. Chim. Acta, **37**, 1080 (1954); J.P. Ryan, P.R. O'Conner: J.Am. Chem. Soc., **74**, 5866 (1952); E.N. Marbell, R. Teranishi: *Ibid.*, **76**, 6165 (1954); H. Conroy, R.A. Firestone: *Ibid.*, **78**, 2290 (1956); D.Y. Curtin, R.J. Crawford: *Ibid.*, **79**, 3156 (1957).

each of which is accompanied by a reversal of the allyl group. Consequently, it is considered that this rearrangement of III to IV proceeds principally through a two-cycle process as shown in Chart 4. This is the first example of out-of-ring migration of an allyl group to an active methyl group.

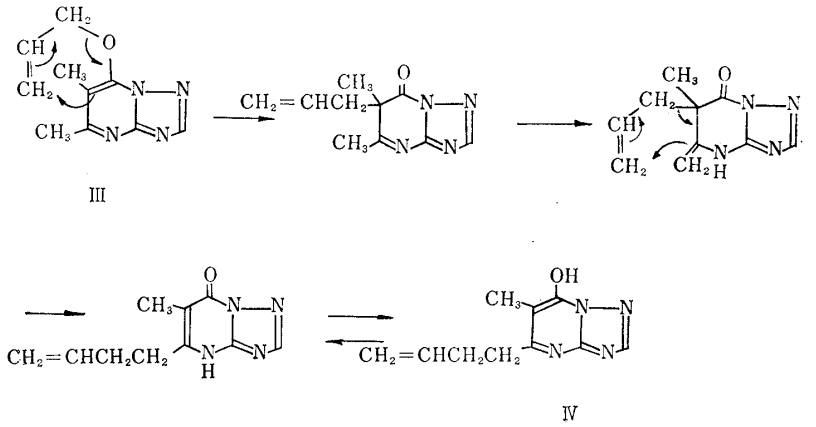


Chart 4.

Experimental*4

7-Chloro-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidine (II)——A solution of 8.4 g. of 5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (I) in 33.6 cc. of $POCl_3$ was heated under reflux for 1.5 hr. and the excess of $POCl_3$ was removed under reduced pressure. The residue was poured into a stirred mixture of crushed ice and NH_4OH. The mixture was extracted with $CHCl_3$ and the combined $CHCl_3$ extracts were dried over $MgSO_4$. Removal of the solvent left 7.4 g. of a pale yellow solid, m.p. 152~153°. Recrystallization from benzene-petr. benzin gave colorless needles, m.p. 155°. *Anal.* Calcd. for $C_7H_7N_4Cl$: C, 46.04; H, 3.81; N, 30.68. Found: C, 45.94; H, 3.95; N, 30.46.

7-Allyloxy-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidine (III)——To a solution of 0.38 g. of Na dissolved in 40 cc. of allyl alcohol, 3 g. of II was added in small portions under stirring and cooling. After stirring at room temperature for 3 hr., the precipitated NaCl was filtered off and the filtrate was evapo rated 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 $MgSO_4$. Removal of the solvent left 3.2 g. of oil, which was purified by alumina chromatography using benzene as eluent to give 3.0 g. of pale yellow oil. *Anal.* Calcd. for $C_{10}H_{12}ON_4$: C, 58.81; H, 5.92; N, 27.44. Found: C, 59.08; H, 6.21; N, 27.15.

Thermal Rearrangement of III——Twenty-five grams of III was heated at 180° for 1 hr., by which III reacted vigorously in the first stage and solidified immediately. The resulting solid was dissolved in $CHCl_3$ and the insoluble crystals were collected by filtration to give 16.6 g. of white crystals (A), m.p. 236~238°. Recrystallization from EtOH gave pure 5-(3-butenyl)-6-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (IV) as colorless prisms, m.p. 241~242°. *Anal.* Calcd. for $C_{10}H_{12}ON_4$: C, 58.81; H, 5.92; N, 27.44. Found: C, 58.67; H, 6.01; N, 27.26. IR: $\nu_{C=O}^{Nujol}$ 1698 cm^{-1} (lactam C=O). UV $\lambda_{max}^{EtOH}m\mu$ (log ε): 242 (3.65), 280 (4.04). This compound was soluble in dil. alkali and insoluble in acid.

The filtrate (the $CHCl_3$-soluble part of the reaction product) was passed through a column of alumina and eluted with benzene-$CHCl_3$ and $CHCl_3$ affording the five fractions. The first fraction eluted with benzene-$CHCl_3$ (5:1) gave a colorless oily substance (B), which was not further characterized. The second fraction eluted with the same solvent gave 5 mg. of colorless pillars (C), m.p. 99~99.5°, on recrystallization from petr. benzin. C was identified with 4-allyl-5-(3-butenyl)-6-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (IVa) by mixed melting point and their IR and UV spectral comparisons. *Anal.* Calcd. for $C_{13}H_{16}ON_4$: C, 63.91; H, 6.60; N, 22.94. Found: C, 64.07; H, 6.81; N, 23.04. The product obtained from benzene-$CHCl_3$ (3:1~1:1) eluate, was recrystallized from benzene to give 810 mg. of colorless scales (D), m.p. 170~171°, which were identified with 4-allyl-5,6-dimethyl-*s*-triazolo[1,5-*a*]-pyrimidin-7(4*H*)-one (Ia) by the mixed melting point determination and their IR and UV spectral comparisons. *Anal.* Calcd. for $C_{10}H_{12}ON_4$: C, 58.81; H, 5.92; N, 27.44. Found: C, 58.95; H, 6.00; N, 27.39. The

*4 All melting points are uncorrected. NMR spectra were measured in deutero-chloroform with a Varian A-60 Analytical NMR spectrometer at 60 Mc. using tetramethylsilane as an internal standard. Infrared spectra were measured with the Kōken Infrared Srectrophotometer, Model DS-301, and ultraviolet spectra were taken with the Hitachi Recording Spectrophotometer, EPS-2.

next product obtained from the same solvent eluate, was recrystallized from benzene-petr. benzin to give 30 mg. of colorless plates (E), m.p. 167~168°, which were identified with 3-allyl-5-(3-butenyl)-6-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-one (IVb) by the mixed melting point determination and their IR and UV spectral comparisons. *Anal.* Calcd. for $C_{13}H_{16}ON_4$: C, 63.91; H, 6.60; N, 22.94. Found: C, 64.12; H, 6.79; N, 22.65. The last product obtained from $CHCl_3$ eluate, was recrystallized from EtOH to give 1.38 g. of colorless scales (F), m.p. 204~205°, which were identified with 3-allyl-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-one (Ib) by the mixed melting point determination and their IR and UV spectral comparisons. *Anal.* Calcd. for $C_{10}H_{12}ON_4$: C, 58.81; H, 5.92; N, 27.44. Found: C, 58.93; H, 5.98; N, 27.35.

5-(3-Butenyl)-6-methyl-7-chloro-*s*-triazolo[1,5-*a*]pyrimidine (V)——A solution of 1.3 g. of IV in 5.2 cc. of $POCl_3$ was heated under reflux for 2 hr. The excess of $POCl_3$ was removed under reduced pressure on a steam bath and the residual syrup was poured into ice water with stirring. The solution was neutralized with conc. NH_4OH and extracted with $CHCl_3$. The extract was washed with H_2O and dried over $MgSO_4$. After removal of the solvent, the residue was dissolved in benzene and purified by chromatography through an alumina column giving 1.05 g. of white crystals. Recrystallization from petr. benzin gave colorless pillars, m.p. 54.5~55°. *Anal.* Calcd. for $C_{10}H_{11}N_4Cl$: C, 53.93; H, 4.97; N, 25.16. Found: C, 53.92; H, 5.14; N, 25.18.

Hydrolysis of V with Aqueous Sodium Hydroxide——A solution of 0.2 g. of V in 4 cc. of 5% NaOH was heated on a steam bath for 10 min. The solution was diluted with H_2O, treated with charcoal, and acidified with 10% HCl. The precipitated crystals were collected by filtration, washed with H_2O, and recrystallized from EtOH to give 0.17 g. of colorless prisms, m.p. 241~242°, which were identified as IV both by admixture and IR spectral comparison.

5-Butyl-6-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (VI)——A solution of 1 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 15 min. After removal of the catalyst, the solvent was distilled off under reduced pressure. The residue was recrystallized from EtOH to give 0.92 g. of colorless pillars, m.p. 191~192°. *Anal.* Calcd. for $C_{10}H_{14}ON_4$: C, 58.28; H, 6.84; N, 27.14. Found: C, 58.43; H, 6.81; N, 26.96. IR: $\nu_{C=O}^{Nujol}$ 1699 cm^{-1} (lactam C=O). UV λ_{max}^{EtOH} mμ (log ε): 245 (3.67), 280.5 (4.03).

5-Methyl-6-butyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (VII)——A mixture of 3.72 g. of ethyl 2-acetylhexanoate and 1.68 g. of 5-amino-*s*-triazole in 5 cc. of AcOH was heated under reflux for 4 hr. After cool, the deposited crystals were collected by filtration, washed with EtOH, and recrystallized from EtOH to give 1.95 g. of colorless needles, m.p. 227~228°. *Anal.* Calcd. for $C_{10}H_{14}ON_4$: C, 58.28; H, 6.84; N, 27.14. Found: C, 58.18; H, 6.86; N, 26.97. UV λ_{max}^{EtOH} mμ (log ε): 247 (3.72), 279.5 (4.04).

5-Methyl-6-isobutyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (VIII)——A mixture of 2.17 g. of ethyl 2-acetyl-4-methylpentanoate and 0.95 g. of 5-amino-*s*-triazole in 4.5 cc. of AcOH was heated under reflux for 4 hr. After cool, the deposited crystals were collected by filtration and recrystallized from EtOH to give 1.05 g. of colorless needles, m.p. 268~269°. *Anal.* Calcd. for $C_{10}H_{14}ON_4$: C, 58.28; H, 6.84; N, 27.14. Found: C, 58.40; H, 7.09; N, 26.98. UV λ_{max}^{EtOH} mμ (log ε): 247 (3.74), 280 (4.02).

Condensation of Ethyl 2-methylacetoacetate with 5-Allylamino-*s*-triazole——a) A mixture of 0.23 g. of ethyl 2-methylacetoacetate and 0.15 g. of 5-allylamino-*s*-triazole was heated at 180° for 30 min. and then at 200° for 1 hr. After cool, the mixture was dissolved in benzene-$CHCl_3$ and separated to two products by alumina chromatography. The first fraction gave 120 mg. of white crystals, m.p. 93~98°, which was recrystallized from petr. benzin to give 4-allyl-6,7-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one (Ic) as colorless pillars, m.p. 101~102°. *Anal.* Calcd. for $C_{10}H_{12}ON_4$: C, 58.81; H, 5.92; N, 27.44. Found: C, 58.93; H, 6.10; N, 27.30. IR: $\nu_{C=O}^{Nujol}$ 1667 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε): 254 (3.77), 272 (3.82). The second fraction gave 7 mg. of 4-allyl-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (Ia) as colorless scales, m.p. 170~171°, on recrystallization from benzene. *Anal.* Calcd. for $C_{10}H_{12}ON_4$: C, 58.81; H, 5.92; N, 27.44. Found: C, 58.94; H, 5.93; N, 27.32. IR: $\nu_{C=O}^{Nujol}$ 1685 cm^{-1}. UV λ_{max}^{Nujol} mμ (log ε): 247 (3.72), 285 (4.12).

b) A mixture of 0.14 g. of ethyl 2-methylacetoacetate and 0.1 g. of 5-allylamino-*s*-triazole in 1 cc. of AcOH was heated under reflux for 6 hr. and the solvent was removed under reduced pressure. The residue was treated as above giving 8 mg. of Ic and 90 mg. of Ia. These products were respectively identical by admixture with the samples (Ic and Ia) obtained by the method a).

Condensation of Ethyl 2-Methylacetoacetate with 3-Amino-4-allyl-4*H*-*s*-triazole——a) A mixture of 1.59 g. of ethyl 2-methylacetoacetate and 0.9 g. of 3-amino-4-allyl-4*H*-*s*-triazole was heated at 180° for 30 min. and then at 200° for 30 min. The reaction mixture was dissolved in benzene-$CHCl_3$ (1:1) and passed through a column of alumina. Elution with benzene-$CHCl_3$ gave two fractions: (1) 3-allyl-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H*)-one (Ib) as colorless scales (40 mg.), m.p. 204~205°, on recrystallization from EtOH. *Anal.* Calcd. for $C_{10}H_{12}ON_4$: C, 58.81; H, 5.92; N, 27.44. Found: C, 58.95; H, 6.12; N, 27.41. IR: $\nu_{C=O}^{Nujol}$ 1671 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε): 253 (3.71), 291.5 (4.10). (2) 3-Allyl-6,7-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-5(3*H*)-one (Id) as colorless plates (60 mg.), m.p. 175~

175.5°, on recrystallization from benzene. *Anal.* Calcd. for $C_{10}H_{12}ON_4$: C, 58.81; H, 5.92; N, 27.44. Found : C, 58.99; H, 6.04; N, 27.35. IR : $\nu_{C=O}^{Nujol}$ 1653 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) : 238 (3.77), 245 (3.72), 270 (3.86).

b) A mixture of 0.69 g. of ethyl 2-methylacetoacetate and 0.5 g. of 3-amino-4-allyl-4*H*-*s*-triazole 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 EtOH to give 0.4 g. of colorless scales, m.p. 204~205°, undepressed on admixture with Ib obtained by the method a).

Allylation of I with Allyl Bromide——To a solution of 5 g. of KOH dissolved in 100 cc. of 85% EtOH, 6.56 g. of finely powdered I and 9 g. of allyl bromide were added and the mixture was heated under reflux for 3 hr. After removal of the solvent under reduced pressure, the residue was dried over P_2O_5 in a desiccator and extracted with $CHCl_3$ under reflux. The $CHCl_3$-insoluble solid was dissolved in H_2O and acidified with 10% HCl to give 0.85 g. of I. The $CHCl_3$ extract was concentrated and chromatographed on alumina. Elution with $CHCl_3$ gave two fractions. The first fraction was recrystallized from benzene to give 1.63 g. of colorless scales, m.p. 170~171°, which was identical in all respects with the sample (Ia). The second fraction was recrystallized from benzene-EtOH to give 2.46 g. of colorless scales, m.p. 204~205°, which was also identical in all respects with the sample (Ib).

Allylation of IV with Allyl Bromide——To a solution of 3.36 g. of KOH in 90 cc. of 90% EtOH, 5.7 g. of IV and then 7.26 g. of allyl bromide were added and the solution was heated under reflux for 3 hr. After removal of the solvent under reduced pressure, the residue was dried over P_2O_5 in a desiccator and extracted with $CHCl_3$(100 cc. × 2) under reflux. The combined extracts were concentrated and the residue was dissolved in benzene-$CHCl_3$ and passed through a column of alumina. Elution with benzene-$CHCl_3$ gave the two kinds of products. The first eluted product was recrystallized from petr. benzin to give 1.38 g. of 4-allyl-5-(3-butenyl)-*s*-triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (IVa) as colorless pillars, m.p. 99~99.5°. *Anal.* Calcd. for $C_{13}H_{16}ON_4$: C, 63.91; H, 6.60; N, 22.94. Found : C, 64.07; H, 6.81; N, 23.04. IR : $\nu_{C=O}^{Nujol}$ 1676 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) : 244 (3.68), 287 (4.12). The second eluted product was recrystallized from benzene-petr. benzin to give 3.18 g. of 3-allyl-5-(3-butenyl)-6-methyl-*s*-triazolo-[1,5-*a*]pyrimidin-7(3*H*)-one (IVb) as colorless plates, m.p. 167~168°. *Anal.* Calcd. for $C_{13}H_{16}ON_4$: C, 63.91; H, 6.60; N, 22.94. Found : C, 64.04; H, 6.79; N, 22.85. IR : $\nu_{C=O}^{Nujol}$ 1674 cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) : 253 (3.69), 292.5 (4.10).

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Summary

The thermal rearrangement of 7-allyloxy-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidine (III) was carried out and five kinds of rearrangement products; 3- and 4-allyl-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidin-7(3*H* and 4*H*)-ones (Ib and Ia), 5-(3-butenyl)-6-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (IV), and its 3- and 4-allyl derivatives (IVb and IVa) were obtained. Among these products, the out-of-ring Claisen rearrangement product (IV) was obtained in 66% yield. This reaction is the first example of out-of-ring migration of an allyl group to an active methyl group.

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