b) A mixture of 0.5 g. of (III) and 2 cc. of Ac_2O was heated on a steam bath for 15 min. and the resulting crystals were collected by filtration, washed with dehyd. EtOH, and dried to 0.68 g. of 14-acetyl-5-acetamidopyrazole, m.p. 190~191°. Recrystallization from dehyd. EtOH gave colorless needles, m.p. 190.5~191.5°. *Anal.* Calcd. for $C_7H_9O_2N_3$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.32; H, 5.57; N, 25.23. IR ν_{max}^{Nujol} cm^{-1}: 1738 (C=O of ring N), 1661 (C=O of amino).

This compound was heated with H_2O on a steam bath for 15 min. After cool, the resulting crystals were collected by filtration and dried to colorless prisms, m.p. 223~224°, which was identified with (XXII) by the mixed melting point determination and the infrared spectral comparison.

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

Summary

Condensation of 1,3-dicarbonyl compounds with 5-aminopyrazole (III) and its 3-carboxylic ester (X) was examined and several kinds of 5,7-disubstituted pyrazolo[1,5-*a*]-pyrimidines were obtained. It was observed by the infrared spectrum that the hydroxyl group at 5- and 7-positions of pyrazolo[1,5-*a*]pyrimidine ring shows the lactam form in the neutral medium,

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101. Yasuo Makisumi: Studies on the Azaindolizine Compounds. XI.*2 Synthesis of 6,7-Disubstituted Pyrazolo[1,5-*a*]pyrimidines.

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

In the foregoing paper*2, the author reported on the synthesis of 5,7-disubstituted pyrazolo[1,5-*a*]pyrimidines by means of the condensation of 1,3-dicarbonyl compounds with 5-aminopyrazole (I) and its derivatives.

In the present paper, the condensation of 2-ethoxymethylene-1,3-dicarbonyl compounds with (I) to give 6,7-disubstituted pyrazolo[1,5-*a*]pyrimidines is described.

Condensation of ethyl 2-cyano-3-ethoxyacrylate with (I) in boiling ethanol gave a product (II), $C_9H_{10}O_2N_4$, m.p. 186°. However, when glacial acetic acid instead of ethanol was used as the solvent, an isomeric compound of (II), m.p. 147°, (III) was obtained. The former showed an absorption band at 311 mμ (log ε 4.37) in the ultraviolet region and absorption bands of the groups ring NH, side chain NH, C≡N, and ester C=O in the infrared region (see Table I). Moreover, (II) was negative for the reaction of the aromatic primary amines using sodium pentacyanoaquoferriate. These results support that the structure of (II) is ethyl 2-cyano-3-(5-pyrazolylamino)acrylate. The latter compound (III) showed absorption bands at 3537, 3373 (NH_2), and 1710 (ester C=O) in the infrared spectrum (in $CHCl_3$) and (III) was identified with the product which obtained by teratment of (II) with boiling glacial acetic acid. Therefore, the structure of (III) was established to be ethyl 7-aminopyrazolo[1,5-*a*]pyrimidine-6-carboxylate. (III) was also

*1 Fukushima-ku, Osaka (牧角徳夫).

*2 Part X. Y. Makisumi: This Bulletin, **10**, 612 (1962).

prepared by heating of (II) with 10% hydrochloric acid, but treatment of (II) with aqueous sodium carbonate afforded 7-hydroxypyrazolo[1,5-*a*]pyrimidine-6-carbonilile (IV).

From these results, it was considered that the reaction of ethyl 2-cyano-3-ethoxyacrylate with (I) ln glacial acetic acid produced (III) by the acidic ring closure of (II) which would produce as an intermediate, and that the ring closure of (II) is predominant at the cyano group in the acidic medium but at the ester group in the alkaline medium.

When (III) was allowed to stand in aqueous sodium hydroxide overnight at room temperature, the corresponding carboxylic acid (V) produced after saponification, but heating of (III) with aqueous sodium hydroxide for three hours afforded 7-hydroxypyrazolo[1,5-*a*]pyrimidine-6-carboxylic acid (VI), which was also obtained by heating of (V) with aqueous sodium hydroxide for two hours.

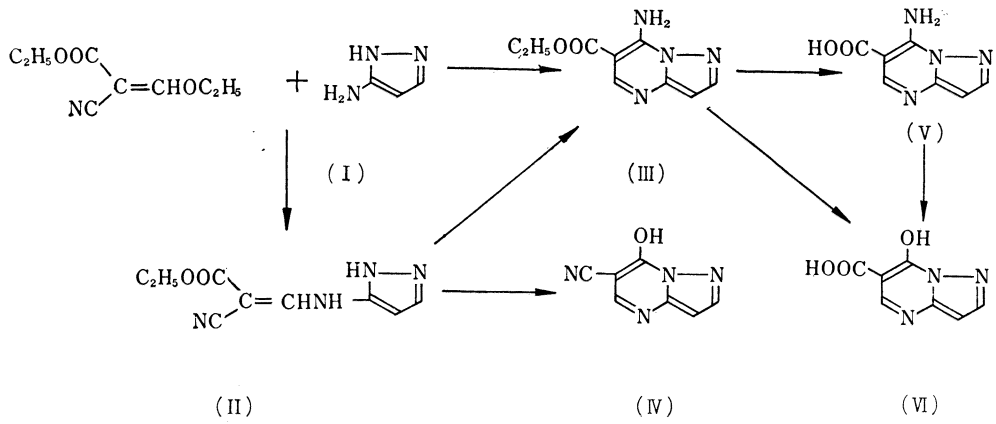


Chart 1.

Reaction of ethoxymethylenemalononitrile with (I) in ethanol or glacial acetic acid occurred exothermically, and 7-aminopyrazolo[1,5-*a*]pyrimidine-6-carbonitrile (VII) was isolated in a theoretical yield. The structure of (VII) was confirmed by the spectral and chemical evidence. Namely, (VII) showed a similar curve to that of (III) in the ultraviolet spectrum and absorption bands of the groups NH_2 and $C\equiv N$ in the infrared spectrum. Moreover, (VII) was hydrolyzed by heating with 40% sulfuric acid for two hours to (V) which was obtained in the foregoing reaction. Analogously, reaction of diethyl ethoxymethylenemalonate with (I) in ethanol or glacial acetic acid at refluxing temperature gave ethyl 7-hydroxypyrazolo[1,5-*a*]pyrimidine-6-carbo xylate (VIII), whose structure was confirmed by the fact that (VIII) was converted to (VI) by saponification with aqueous sodium hydroxide.

Reaction of ethyl 2-acethyl-3-ethoxyacrylate with (I) in ethanol or glacial acetic acid occurred exothermically and a product (IX), m.p. 94.5~95.5°, was isolated in a good yield, whose structure was assigned to be ethyl 7-methylpyrazolo[1,5-*a*]pyrimidine-6-carboxylate on the basis of the following experiments. (IX) was converted to the corresponding carboxylic acid (X) by saponification with aqueous sodium hydroxide, which was decarboxylated to a methylpyrazolo[1,5-*a*]pyrimidine (XI) by treatment with boiling 40% sulfuric acid. On the other hand, 5-methylpyrazolo[1,5-*a*]pyrimidin-7-ol*[1] (XII) was chlorinated to the corresponding 7-chloro derivative (XIII) by the action of phosphoryl chloride, which was dehalogenated by catalytic reduction into 5-methylpyrazolo[1,5-*a*]pyrimidine (XIV). These methyl derivatives (XI and XIV) showed similar curves in each ultraviolet spect- rum, but these compounds were not identified with each other. Therefore, it was decided that (XI) is 7-methylpyrazolo[1,5-*a*]pyrimidine and its original compound (IX) is ethyl 7-methylpyrazolo[1,5-*a*]pyrimidine-6-carboxylate.

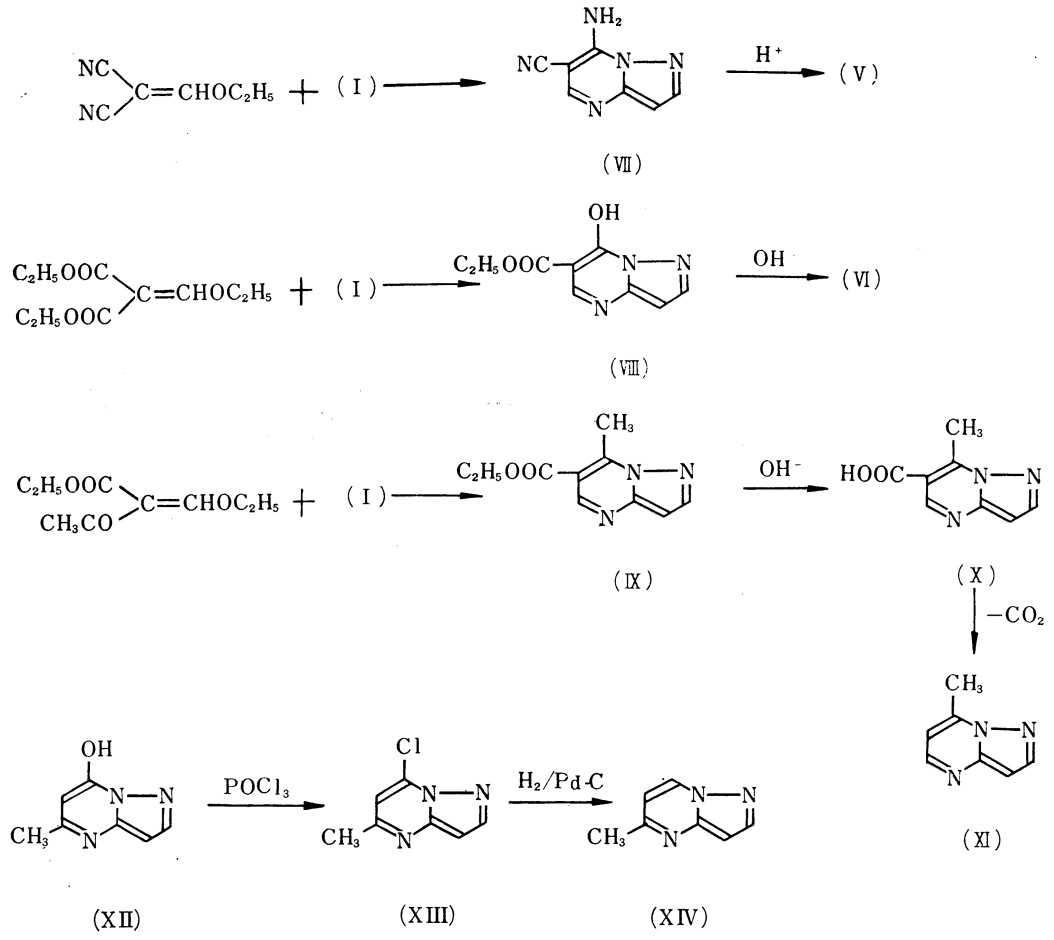


Chart 2.

In order to compare with these reaction of ring-formation of pyrazolo[1,5-*a*]pyrimidine, the condensation of 2-ethoxymethylene-1,3-dicarbonyl compounds with 1-phenyl-5-aminopyrazole (XV) was examined. Consequently, it was clear that these condensation proceeded only between the ethoxymethylene group and the amino group of (XV), and the ring closure to pyrazolo[3,4-*b*]pyridine did not occur.

Namely, reaction of ethyl 2-cyano-3-ethoxyacrylate with (XV) in ethanol or glacial acetic acid at boiling temperatures for one hour gave only ethyl 2-cyano-3-(1-phenyl-5-pyrazolylamino)acrylate (XVI) and the ring closure of (XVI) to pyrazolo[3,4-*b*]pyridine derivative did not occur, although heating at boiling temperature was continued for long time. Analogously, reaction of diethyl ethoxymethylenemalonate and ethyl 2-acetyl-3-ethoxyacrylate with (XV) was carried out under the same reaction conditions, and diethyl (1-phenyl-5-pyrazolyl)aminomethylenemalonate (XVII) and ethyl 2-acetyl-3-(1-phenyl-5-pyrazolylamino)acrylate (XVIII) were obtained. The structure of these products (XVI, XVII, and XVIII) were confirmed by the spectral evidences (see Table I).

From these results, it was clear that the condensation of 2-ethoxymethlene-1,3-dicarbonyl compounds with 5-aminopyrazole (I) did first occur between the ethoxy-

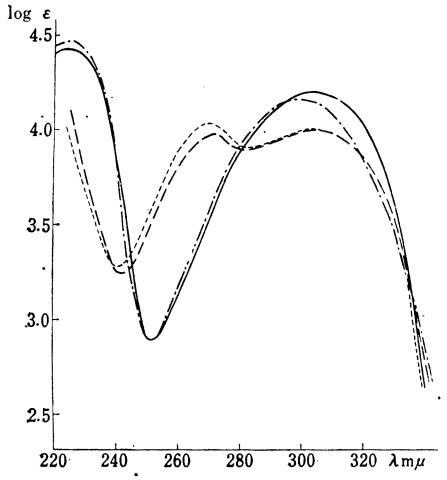
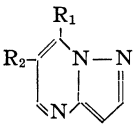


Fig. 1. Ultraviolet Absorption Spectra (in EtOH)



——— (III) $R_1=NH_2$, $R_2=COOC_2H_5$
– – – (IV) $R_1=OH$, $R_2=CN$
-·-·- (VII) $R_1=NH_2$, $R_2=CN$
····· (VIII) $R_1=OH$, $R_2=COOC_2H_5$

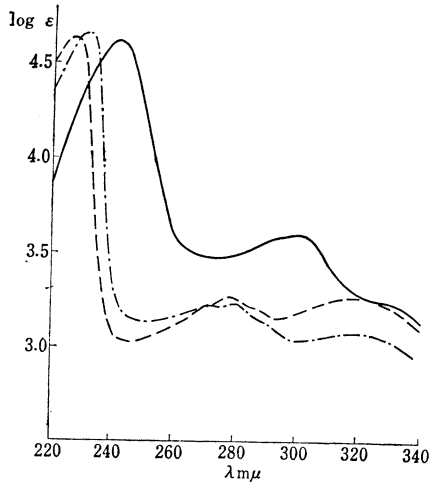
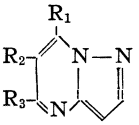


Fig. 2. Ultraviolet Absorption Spectra (in EtOH)



——— (IX) $R_1=CH_3$, $R_2=COOC_2H_5$, $R_3=H$
– – – (XI) $R_1=CH_3$, $R_2=R_3=H$
-·-·- (XIV) $R_1=R_2=H$, $R_3=CH_3$

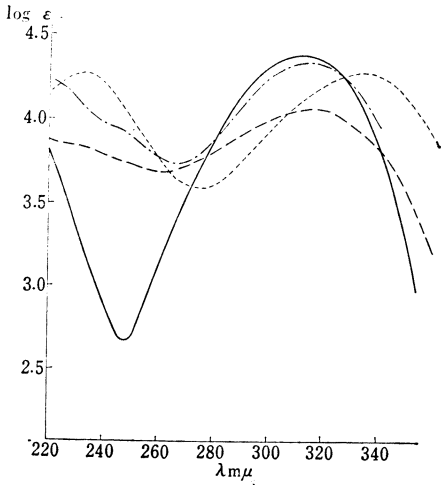
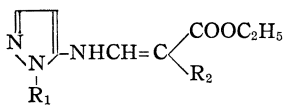


Fig. 3. Ultraviolet Absorption Spectra (in EtOH)



——— (II) $R_1=H$, $R_2=CN$
– – – (XVI) $R_1=C_6H_5$, $R_2=CN$
-·-·- (XVII) $R_1=C_6H_5$, $R_2=COOC_2H_5$
····· (XVIII) $R_1=C_6H_5$, $R_2=COCH_3$

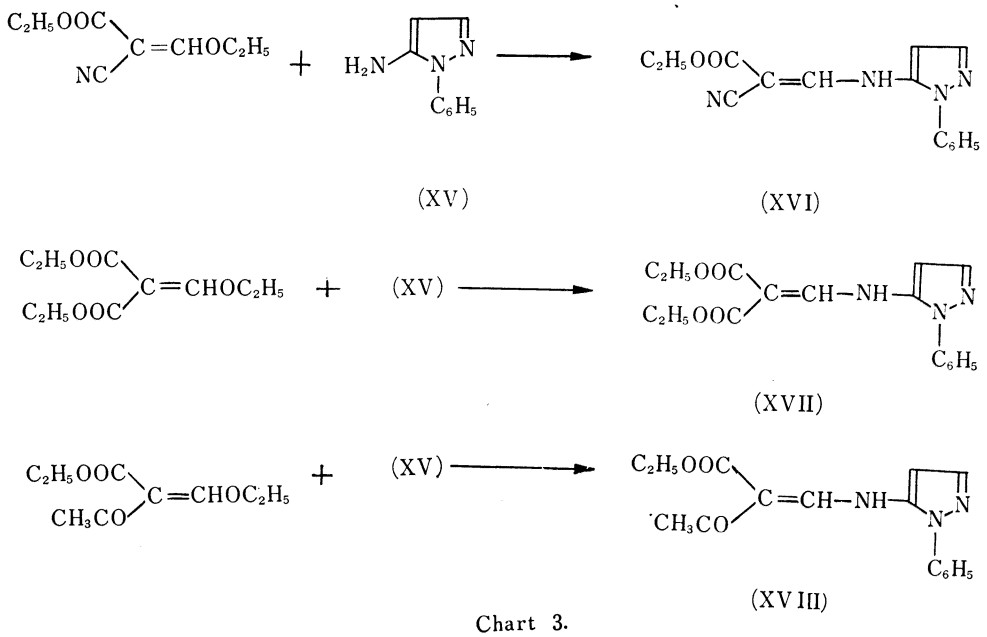


Chart 3.

TABLE I. Infrared Spectra of the 5-Aminopyrazole Derivatives ($\nu_{max}^{CHCl_3}$ in cm^{-1})

Compd.	Ring NH	Side chain NH	C≡N	C=O	C=C	NH_2[b]
(II)[a]	3329	3190	2245	1712	1631	—
(XVI)	—	3245	2238	1680	1633	—
(XVII)	—	3256	—	1702	1615	—
(XVIII)	—		—	1702	1637	—

a) in Nujol

b) All compounds were negative for the reaction of the aromatic primary amines using sodium pentacyanoaquoferriate.

methylene group and the amino group and the interaction of the carbonyl group and NH group of pyrazole ring followed to form pyrazolo[1,5-*a*]pyrimidine ring.

From the same point of view as the preceding work*[1], the infrared spectrum of the 7-hydroxy- and 7-aminopyrazolo[1,5-*a*]pyrimidine derivatives which obtained here, were measured. Consequently, it was observed that the hydroxyl group at 7-position showed the lactam form and the amino group at 7-position showed the amino form in the neutral medium. These results is identical with those of the preceding work.*[1]

Experimental*[3]

Ethyl 2-Cyano-3-(5-pyrazolylamino)acrylate (II)——A mixture of 0.85 g. of ethyl 2-cyano-3-ethoxyacrylate and 0.41 g. of (I) in 8 cc. of dehyd. EtOH was refluxed for 30 min. After cool, the resulting crystals were collected by filtration and recrystallized from EtOH to 0.98 g. of colorless needles, m.p. 186°. *Anal.* Calcd. for $C_9H_{10}O_2N_4$: C, 52.43; H, 4.85; N, 27.18. Found : C, 52.26; H, 5.15; N, 27.03. UV : λ_{max}^{EtOH} 311 mμ (log ε 4.37). IR : see Table I.

Ethyl 7-Aminopyrazolo[1,5-*a*]pyrimidine-6-carboxylate (III)——a) A mixture of 0.85 g. of ethyl 2-cyano-3-ethoxyacrylate and 0.41 g. of (I) in 10 cc. of AcOH was refluxed for 30 min. The reaction mixture was concentrated in a reduced pressure to dryness and the residue was diluted with H_2O and basified with 5% NaOH. The resulting crystals were collected by filtration and recrystallized from 70% EtOH to give 0.93 g. of colorless needles, m.p. 147°. *Anal.* Calcd. for $C_9H_{10}O_2N_4$: C, 52.43;

*3 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.

H, 4.85; N, 27.18. Found: C, 52.55; H, 5.08; N, 27.06. UV λ_{max}^{EtOH} mμ (log ε): 225 (4.44), 306 (4.21). IR $\nu_{max}^{CHC_{13}}$ cm^{-1}: 3537, 3373 (NH_2), 1710 (ester C=O).

b) A solution of 2 g. of (II) in 10 cc. of AcOH was refluxed for 1 hr. The reaction mixture was treated by the same method as above and the resulting product was recrystallized from 70% EtOH to give 1.63 g. of colorless needles, m.p. 147°, which was identified with the sample prepared by method (a) by the mixed melting point and the infrared spectra.

c) A mixture of 0.5 g. of (II) and 5 cc. of 10% HCl was heated on a steam bath for 1 hr. After cool, the reaction solution was neutralized with 10% NaOH, the precipitated crystals were collected by filtration, washed with H_2O, and recrystallized from 70% EtOH to give 0.46 g. of colorless needles, m.p. 147°, which was also identified with the samples described in (a) and (b), by the mixed melting point and the infrared spectra.

7-Hydroxypyrazolo[1,5-*a*]pyrimidine-6-carbonitrile (IV)——A mixture of 0.5 g. of (II) and 10 cc. of 10% Na_2CO_3 was warmed for 15 min. forming a clear solution. The solution was acidified with AcOH and the resulting precipitate was collected by filtration, washed with H_2O, and recrystallized from 50% EtOH to give 0.4 g. of colorless needles, m.p. above 340°. *Anal.* Calcd. for $C_7H_4ON_4$: C, 52.50; H, 2.50; N, 35.00. Found: C, 52.23; H, 2.60; N, 35.07. UV λ_{max}^{EtOH} mμ (log ε): 272 (4.00), 305 (4.02). IR ν_{max}^{Nujol} cm^{-1}: 2238 (C≡N), 1669 (lactam C=O).

7-Aminopyrazolo[1,5-*a*]pyrimidine-6-carboxylic Acid (V)——a) A suspension of 0.5 g. of (III) in 10 cc. of 10% NaOH was allowed to stand overnight at room temperature forming a clear solution. The solution was filtered and the filtrate was acidified with AcOH giving the precipitated crystals, which were collected by filtration, washed with H_2O, and recrystallized from 50% EtOH to give 0.4 g. of colorless needles, m.p. 242°(decomp.). *Anal.* Calcd. for $C_7H_6O_2N_4$: C, 47.19; H, 3.37; N, 31.46. Found: C, 46.92; H, 3.57; N, 31.21. UV λ_{max}^{EtOH} mμ (log ε): 224 (4.38), 302 (4.14). IR ν_{max}^{Nujol} cm^{-1}: 3583 (acid OH), 3311, 3216 (NH_2), 1662 (acid C=O).

b) A mixture of 0.15 g. of (VII) and 2 cc. of 40% H_2SO_4 was refluxed for 1.5 hr. After cool, the reaction solution was adjusted to pH 5~6 with 10% NaOH, the precipitated crystals were collected by filtration, washed with H_2O, and recrystallized from 50% EtOH to give 0.85 g. of colorless needles, m.p. 242°(decomp.), which was identified with the sample prepared in (a), by the infrared spectral comparison.

7-Hydroxypyrazolo[1,5-*a*]pyrimidine-6-carboxylic Acid (VI)——a) A mixture of 0.3 g. of (III) and 3 cc. of 10% NaOH was heated on a steam bath for 3 hr., when NH_3 gas evolved. After cool, the precipitated Na salt was collected by filtration, dissolved in H_2O, and acidified with AcOH to give 0.27 g. of white crystals, Recrystallization from 50% EtOH gave white needles, m.p. 319~320° (decomp.). *Anal.* Calcd. for $C_7H_5O_3N_3$: C, 46.92; H, 2.79; N, 23.46. Found: C, 46,85; H, 3.06; N, 23.34. IR ν_{max}^{Nujol} cm^{-1}: 1732 (acid C=O), 1675 (lactam C=O).

b) A mixture of 0.5 g. of (V) and 5 cc. of 10% NaOH was heated on a steam bath for 2 hr., when NH_3 gas evolved. The reaction mixture was treated as above and the resulting crystals were recrystallized from 50% EtOH to give 0.38 g. of white needles, m.p. 319~320°(decomp.), which was identified with the sample prepared in (a) by the infrared spectral comparison.

c) A mixture of 1.0 g. of (VIII) and 10 cc. of 10% NaOH was heated on a steam bath for 3 hr. The reaction mixture was treated as above giving 0.7 g. of white needles, m.p. 319~320°(decomp.), which was identified with the samples prepared in (a) and (b) by the infrared spectral comparison.

7-Aminopyrazolo[1,5-*a*]pyrimidine-6-carbonitile (VII)——a) A mixture of 0.61 g. of ethoxymethylenemalononitrile and 0.42 g. of (I) in 6 cc. of AcOH was heated on a steam bath for 20 min. After cool, the resulting crystals were collected by filtration, washed with EtOH, and recrystallized from 50% EtOH to 0.85 g. of white scales, m.p. 302~303°. *Anal.* Calcd. for $C_7H_5N_5$: C, 52.83; H, 3.14; N, 44.03. Found: C, 52.62; H, 3.32; N, 44.15. UV λ_{max}^{EtOH} mμ (log ε): 224 (4.49), 229 (4.16). IR ν_{max}^{Nujol} cm^{-1}: 3314, 3152 (NH_2), 2235 (C≡N).

b) A mixture of 0.3 g. of ethoxymethylenenmalononitrile and 0.21 g. of (I) in 5 cc. of dehyd. EtOH was refluxed for 20 min. and the reaction mixture was treated by the same method as above giving 0.41 g. of white scales, m.p. 302~303°, undepressed on admixture with the sample obtained by the method (a).

Ethyl 7-Hydroxypyrazolo[1,5-*a*]pyrimidine-6-carboxylate (VIII)——A mixture of 5.25 g. of diethyl ethoxymethylenemalonate and 2 g. of (I) in 20 cc. of AcOH was refluxed for 2 hr. After cool, the resulting crystals were collected by filtration, washed with EtOH, and dried to give 4.95 g. of white crystalline powder. Recrystallization from 50% EtOH gave white needles, m.p. 291~292° (decomp.). *Anal.* Calcd. for $C_9H_9O_3N_3$: C, 52.17; H, 4.35; N, 20.28. Found: C, 52.27; H, 4.62; N, 20.09. UV λ_{max}^{EtOH} mμ (log ε): 271 (4.04), 305 (402). IR ν_{max}^{Nujol} cm^{-1}: 1721 (ester C=O), 1669 (lactam C=O).

Ethyl 7-Methylpyrazolo[1,5-*a*]pyrimidine-6-carboxylate (IX)——A mixture of 0.6 g. of ethyl 2-acetyl-3-ethoxyacrylate and 0.25 g. of (I) in 5 cc. of AcOH was heated on a steam bath for 30 min. After cool, the reaction mixture was diluted with H_2O and the resulting crystals were collected by filtration and recrystallized from 50% EtOH to give 0.59 g. of colorless pillars, m.p. 94.5~95.5°.

Anal. Calcd. for $C_{10}H_{11}O_2N_3$: C, 58.54; H, 5.37; N, 20.49. Found: C, 58.75; H, 5.37; N, 20.39. UV: λ_{max}^{EtOH} mμ(log ε): 241(4.61), 300(3.56).

7-Methylpyrazolo[1,5-*a*]pyrimidine-6-carboxylic Acid (X)——A mixture of 0.5 g. of (IX) and 5 cc. of 10% NaOH was heated on a steam bath for 3 hr. After cool, the reaction mixture was acidified with 10% HCl, the resulting precipitate was collected by filtration, washed with H_2O, and recrystallized from H_2O to give 0.45 g. of white needles, m.p. 240~240.5°(decomp.). *Anal.* Calcd. for $C_8H_7O_2N_3$: C, 54.24; H, 3.95; N, 23.73. Found: C, 54.42; H, 3.95; N, 23.87.

7-Methylpyrazolo[1,5-*a*]pyrimidine (XI)——a) A mixture of 1 g. of (X) and 5 cc. of 40% H_2SO_4 was refluxed for 6 hr. and the reaction mixture was basified with 15% NaOH. The separated oil was extracted with $CHCl_3$ and the extract was washed with H_2O and dried over Na_2SO_4. After evaporation of $CHCl_3$, the residue was purified by chromatography through an alumina column with benzene and 0.58 g. of crystals, m.p. 56~58°, was obtained. Recrystallization from petr. benzin gave colorless pillars, m.p. 59~60°. *Anal.* Calcd. for $C_7H_7N_3$: C, 63.14; H, 5.30; N, 31.56. Found: C, 62.98; H. 5.31; N, 31.71. UV λ_{max}^{EtOH} mμ(log ε): 228(4.64), 278.5(3.27), 318(3.28).

b) (XI) was obtained from 2 g. of (IX) by the same procedure as (a). Colorless pillars (0.6 g.), m.p. 59~60°.

5-Methyl-7-chloropyrazolo[1,5-*a*]pyrimidine (XIII)——A mixture of 3 g. of 5-methyl-7-hydroxypyrazolo[1,5-*a*]pyrimidine*1 (XII) and 15 cc. of $POCl_3$ was heated at 120° for 2 hr. The excess $POCl_3$ was removed in a reduced pressure on a steam bath and the residual syrup was poured with stirring into ice-water. The solution was neutralized with conc. NH_4OH and extracted with $CHCl_3$, the extract was washed with H_2O, and dried over $CaCl_2$. After evaporation of $CHCl_3$, the residue was dissolved in benzene and purified by Al_2O_3 chromatography giving 0.92 g. of colorless needles, m.p. 38~39°. Recrystallization from petr. benzin gave colorless needles, m.p. 38.5~39.5°. *Anal.* Calcd. for $C_7H_6N_3Cl$: C, 50.16; H, 3.60; N, 25.07. Found: C, 50.24; H, 3.74; N, 25.14.

5-Methylpyrazolo[1,5-*a*]pyrimidine (XIV)——A solution of 0.3 g. of (XIII) in 20 cc. of dehyd. EtOH was hydrogenated over 0.15 g. of 5% Pd-C and 0.14 g. of AcONa. One mole of H_2 was absorbed during 30 min. After removal of the catalyst, the filtrate was evaporated to dryness in a reduced pressure and the residue was dissolved in H_2O, and extracted with $CHCl_3$. Evaporation of the solvent gave 0.26 g. of white solid, which was recrystallized from ligroin to 0.19 g. of colorless needles, m.p. 123~124°. *Anal.* Calcd. for $C_7H_7N_3$: C, 63.14; H, 5.30; N, 31.56. Found: C, 62.91; H, 5.57; N, 31.35. UV λ_{max}^{EtOH} mμ(log ε): 229(4.65), 232.5(4.66), 280(3.23), 318(3.07).

Ethyl 2-Cyano-3-(1-phenyl-5-pyrazolylamino)acrylate (XVI)——A mixture of 3.4 g. of ethyl 2-cyano-3-ethoxyacrylate, 3.2 g. of (XV), and 15 cc. of dehyd. EtOH was refluxed for 1 hr. After cool, the resulting crystals were collected by filtration, washed with EtOH, and dried to 4.8 g. of white solid, which was recrystallized from EtOH giving colorless needles, m.p. 167~169°. *Anal.* Calcd. for $C_{15}H_{14}O_2N_4$: C, 63.82; H, 5.00; N, 19.85. Found: C, 63.95; H, 5.05; N, 20.07. UV: λ_{max}^{EtOH} 315 mμ(4.03). IR: see Table I. This compound was also obtained by the same reaction using AcOH instead of EtOH as the solvent.

Diethyl (1-Phenyl-5-pyrazolyl)aminomthylenemalonate (XVII)——A mixture of 1.1 g. of diethyl ethoxymethylenemalonate and 0.8 g. of (XV) in 5 cc. of dehyd. EtOH was refluxed for 3 hr. and the resulting crystals were treated as above. Recrystallization from ligroin gave 1.26 g. of white needles, m.p. 105°. *Anal.* Calcd. for $C_{17}H_{19}O_4N_3$: C, 61.99; H, 5.82; N, 12.76. Found: C, 62.17; H, 6.08; N, 12.77. UV: λ_{max}^{EtOH} 315 mμ(log ε 4.33). IR: see Table I. This compound was also obtained by the same reaction using AcOH instead of EtOH as the solvent.

Ethyl 2-Acetyl-3-(1-phenyl-5-pyrazolylamino)acrylate (XVIII)——A mixture of 1.9 g. of ethyl 2-acetyl-3-ethoxyacrylate, 1.6 g. of (XV), and 10 cc. of dehyd. EtOH was refluxed for 1 hr. and the resulting crystals were treated as above. Recrystallization from EtOH gave 1.95 g. of colorless needles, m.p. 114~115°. *Anal.* Calcd. for $C_{16}H_{17}O_3N_3$: C, 64.20; H, 5.72; N, 14.04. Found: C, 64.18; H, 5.67; N, 14.22. UV λ_{max}^{EtOH} mμ(log ε): 232.5(4.27), 335(4.26). IR: see Table I. This compound was also obtained by the same reaction using AcOH instead of EtOH as the solvent.

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Summary

Condensation of 2-ethoxymethylene-1,3-dicarbonyl compounds with 5-aminopyrazole (I) was examined and several kinds of 6,7-disubstituted pyrazolo[1,5-*a*]pyrimidines were obtained. In the reaction of ethyl 2-cyano-3-ethoxyacrylate with (I), ethyl 2-cyano-3-(5-pyrazolylamino)acrylate (II) as the intermediate was isolated.

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