Studies on the Syntheses of Heterocyclic Compounds. CDXCI (1) Pyrimidine Derivatives V (2). Abnormal Condensation Products of 4-Amino-6-chloro-2-methoxypyrimidine with *p*-Nitrobenzenesulfonyl Chloride

Kiyoshi Okui, Kiyohiko Ito, Masuo Koizumi, Keiichiro Fukumoto, and Tetsuji Kametani (3)

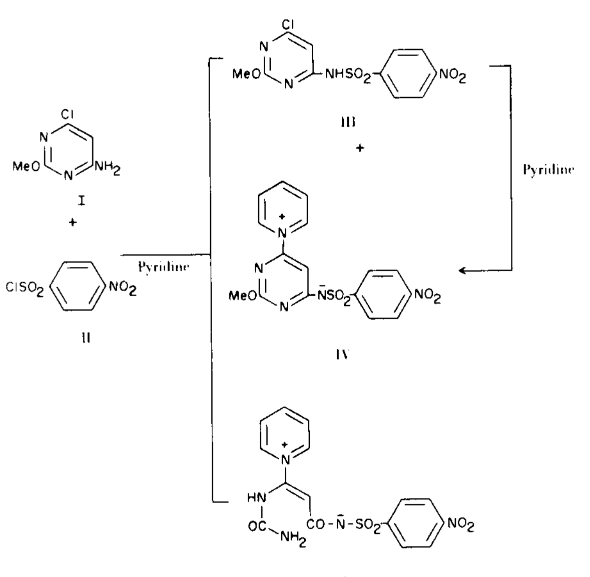
Research Laboratories, Chugai Pharmaceutical Co. Ltd., Takada, Toshimaku, Tokyo, Japan and
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai, Japan

Received April 17, 1972

Condensation of 4-amino-6-chloro-2-methoxypyrimidine (I) with *p*-nitrobenzenesulfonyl chloride (II) gave, in addition to 6-chloro-2-methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine (III), two abnormal by-products, the structures of which were assigned as 1-[2-methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine-6-yl]pyridinium *N*,*N*-betaine (IV) and *N*-(*p*-nitrobenzenesulfonyl)-β-ureido-β-pyridinium acrylamide *N*,*N*-betaine (V).

In the previous paper (2), we reported that condensation of 4-amino-6-chloro-2-methoxypyrimidine (I) with *p*-nitrobenzenesulfonyl chloride (II) in the presence of pyridine afforded the expected 6-chloro-2-methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine (III) besides by-products IV, m.p. 240° dec. and V, m.p. 243-245° dec., the structures of which were unclear. We now wish to describe the elucidation of both abnormal products IV and V.

Scheme 1



The yields of the products III, IV, and V in this condensation based on reaction time are shown in Table I from the point of the reaction time. Examination of Table I shows that an increase in reaction time leads to the decrease of III and an increase of IV, which indicates that product III was converted to IV. When III was heated in pyridine, IV was obtained in good yield.

Scheme 2

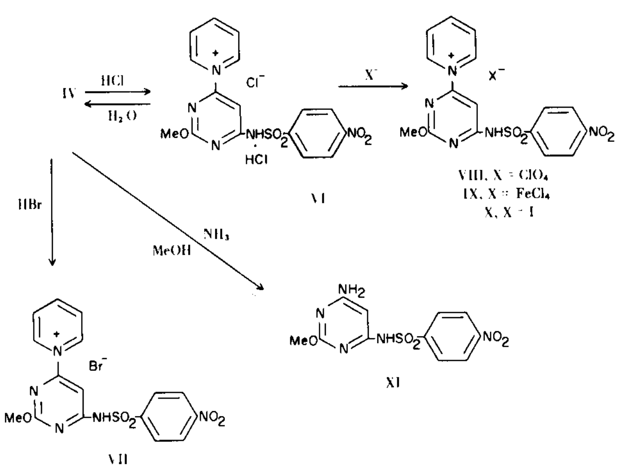


TABLE I

The Relation Between Yields (%) of III, IV, and V and Reaction Times

Compounds Reaction Time (hr)	III	IV	V	Total
5	21.6	7.8	25.3	54.7
15	28.4	21.7	24.4	74.5
40	15.2	35.4	19.5	70.1
80	11.4	45.0	14.6	71.0
160	3.8	58.9	8.2	70.9

To begin with, heating of the yellow compound IV, $C_{16}H_{13}N_5O_5S$ with 10% hydrochloric acid gave the hydrochloride VI (4), which however dissociated back to the free base IV upon addition of water. Treatment of IV with 10% aqueous sodium hydroxide gave a dark brown resinous product (5). Heating of IV with dilute hydrochloric acid in a sealed tube at 150° afforded *p*-nitrobenzenesulfonamide, pyridine and ammonium chloride, indicating the presence of pyridine and *p*-nitrobenzenesulfonyl moieties in the structure. The structure of the pyridinium betaine IV was further supported by the fact that the betaine of *p*-nitrobenzenesulfonyl-ω-pyridinium acetamide had been obtained by treatment of *N*-chloroacetyl-*p*-nitrobenzenesulfonamide with pyridine at 100-110° (6). In 20% hydrobromic acid, compound IV gave the pyridinium bromide VII. Treatment of the above chloride VI with perchloric acid, potassium iodide or ferric chloride gave the corresponding perchlorate VIII, iodide X (7), or chloroferrate IX (8), respectively. Reaction of IV with ammonia in methanol gave 6-amino-2-methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine (XI), which was also obtained by treatment of III with ammonia.

The ir spectrum of IV showed a strong absorption at 1135 cm^{-1} due to the sulfone group, which indicated the imino form of the amino group. According to the observation by Uno (9,10), the amide group of a sulfonamide derivative has an imino structure and the absorption of the sulfone group appears at a lower frequency than 1145 cm^{-1}, and *vice versa.* Other significant absorptions are shown as follows: the band due to the C=N bond of pyrimidine was observed at 1610 cm^{-1} and the nitro group at 1520 cm^{-1}. An X-ray crystallographic study of a single crystal revealed the above compound IV in a monoclinic space group $P2_1/n$ (systematic absences: $h + l = 2n$ in $h0l$, $k = 2n$ in $0k0$) with four molecules (asymmetric units) in a unit cell dimensions $a = 20.40$, $b = 6.11$, $c = 12.94$ Å, and $\beta = 93.0°$ ($V = 1610$ Å^3). The molecular weight (385.5), obtained from the observed density (1.59 g. cm^{-1}) agreed with the value (mol. wt. = 387) calculated with the formula unit of $C_{16}H_{13}N_5O_5S$ as an asymmetric unit.

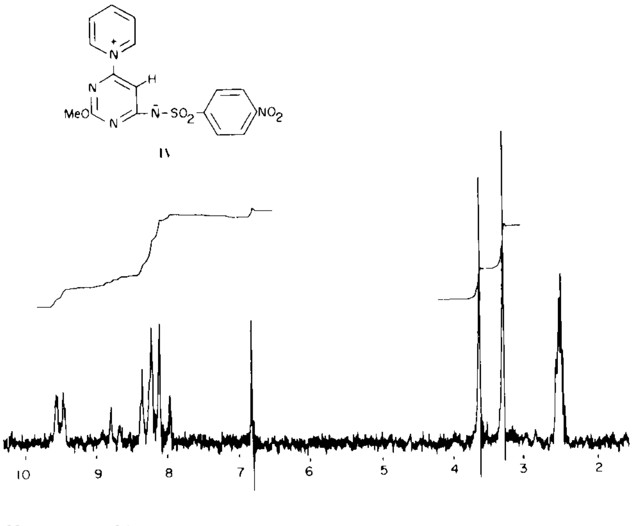


Figure 1. Nmr spectrum of IV in deuteriodimethylsulfoxide.

The nmr spectrum (δ) of IV in deuteriodimethylsulfoxide showed the signals at 3.66 (3H, singlet, OCH_3), 6.85 (1H, singlet, H_5 of pyrimidine), 8.85 and 9.56 ppm (1H, and 2H, triplet and quartet, H_4 and $H_{2,6}$ of pyridine). On the other hand, the nmr spectrum in deuteriotrifluoroacetic acid revealed the aromatic protons at 7.63 (1H, singlet, H_5 of pyrimidine), 8.95 (1H, distorted triplet, H_4 of pyridine) and 9.50 (2H, quartet, $H_{2,6}$ of pyridine). Solvent effect indicated that the proton shifting to down field could be assigned to C_5-H on pyrimidine and the compound (VI) had a betaine form.

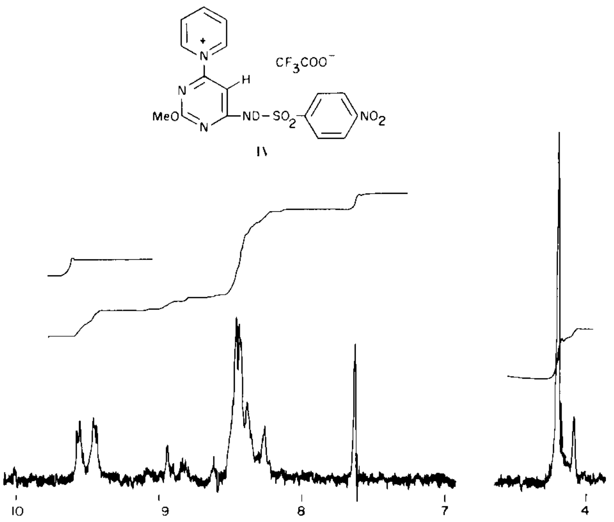


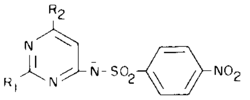
Figure 2. Nmr spectrum of IV in deuterioacetic acid.

This type of *N,N*-betaine has been reported in the past, along with the recent synthesis of 1-(2-substituted 6-arylsulfonamidopyrimidine-4-yl)pyridinium inner salts (11), which have the same skeleton as IV.

In order to examine the generality of the reaction, I was condensed with various sulfonyl halides in the presence of different bases at room temperature. The condensation of I with benzenesulfonyl chloride in pyridine gave the corresponding normal sulfonamide XII without giving the betaine. The reaction of I with *o*-nitrobenzenesulfonyl chloride in pyridine gave the starting material. Replacement of pyridine with trimethylamine afforded the *N,N*-betaine XIII. The reaction of I in 4-picoline or 2,4-lutidine proceeded violently to give a resinous product.

TABLE II

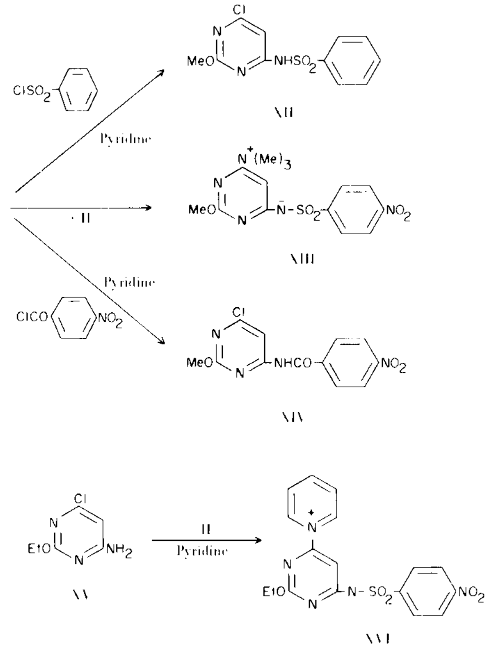
The Appearance of Various Betaines



	R_1	R_2	M.p.° dec.	Appearance	Recryst. Solvent
IV	CH_3O	pyridinium group	240	yellow prisms or fine needles	70% C_2H_5OH
VI	CH_3O	pyridinium group	270	colorless needles (2HCl salt)	10% HCl
VII	CH_3O	pyridinium group	220	colorless prisms (HBr salt)	20% HBr
VIII	CH_3O	pyridinium group	220	colorless needles ($HClO_4$ salt)	dil. CH_3OH
IX	CH_3O	pyridinium group	174	yellow prisms ($HCl{\cdot}FeCl_3$ salt)	CH_3COOH
X	CH_3O	pyridinium group	290	yellow prisms (HI salt)	70% C_2H_5OH
XIII	CH_3O	trimethylammonium group	218	yellow prisms	CH_3OH
XVI	C_2H_5O	pyridinium group	216	yellow prisms	70% C_2H_5OH

This fact is due to the removal of the acidic methyl proton of the pyridinium compound by the pyridine base, resulting in the formation of reactive cyclic enamines. The reaction of I with *p*-nitrobenzoyl chloride in pyridine afforded the benzamide XIV. The condensation of the 2-ethoxypyrimidine XV with *p*-nitrobenzenesulfonyl chloride in pyridine also gave the *N*,*N*-betaine XVI. In the above reaction, the higher reaction temperature might cause the elimination of the methyl group of the methoxypyrimidines resulting in reaction products.

Scheme 3



The pale yellow compound V, $C_{15}H_{13}N_5O_6S$, m.p. 243-245° dec., decomposed in 10% sodium hydroxide to give a brown resinous material. The ir spectrum of V shows the following absorptions: 3370 (NH), 3175 (amide

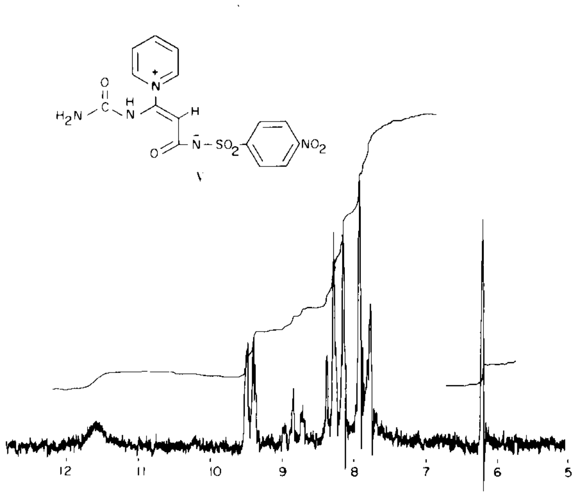
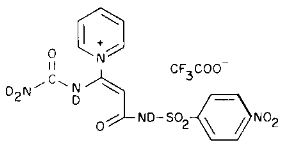


Figure 3. Nmr spectrum of V in deuteriodimethylsulfoxide.

NH), 1710 (CO), 1630 (amide CO), 1595 (amide CO), 1122 (SO_2), 1515 and 1352 (NO_2), and 855 cm^{-1} (1,4-disubstituted benzene). The nmr spectrum (δ) of V in deuteriodimethylsulfoxide showed no signal in the higher field indicating the absence of alkyl protons. In the lower field, there were observed five pyridyl protons (2:1:2) and four phenyl protons. The signal at 7.9 (2H) and 11.5 ppm (1H, broad), which disappeared by addition of deuterium oxide, was assigned to the carboxamide protons of the $CONH_2$ and CONH groups of urea. Moreover, an olefinic proton was observed at 6.20, which was shifted to 7.15 in deuteriotrifluoroacetic acid as in the case of compound IV.



V

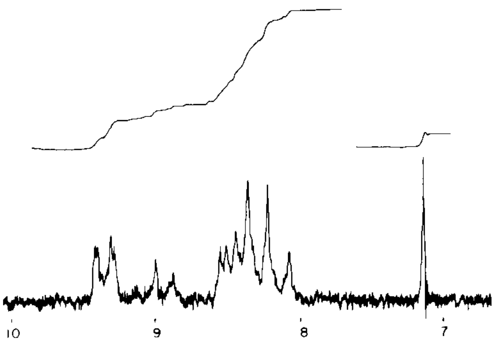


Figure 4. Nmr spectrum of V in deuterioacetic acid.

Hydrogenation of V in the presence of Adams' catalyst gave, after an uptake of 7 moles of hydrogen, an extremely soluble material in water, which was acetylated to give a resinous substance. Furthermore, treatment of V with nitrous acid gave *p*-nitrobenzenesulfonamide, during which an evolution of nitrogen and carbon dioxide was observed and the odor of pyridine was detected. These facts also support the structure of V.

EXPERIMENTAL (12)

Reaction of 4-Amino-6-chloro-2-methoxypyrimidine (I) with *p*-Nitrobenzenesulfonyl Chloride (II).

To a solution of 4.0 g. (0.025 mole) of I in 6 ml. of dry pyridine was added 5.5 g. (0.025 mole) of II. The resulting reddish-orange solution was allowed to stand at room temperature for 20 hours to give a reddish brown viscous oil, which was diluted with 100 ml. of water. From the resulting mixture upon standing crystals separated, which were collected by filtration, washed with water and dried to give 7.0 g. of a solid, m.p. 105-125°. This material was extracted with 70 ml. of hot ethanol in order to remove an insoluble substance IV. After removal of the solvent, the residue was acidified with 30 ml. of concentrated hydrochloric acid and the mixture was heated at 70-80° for a few minutes. After cooling, the crystals which separated were collected to give 1.2 g. (15.2%) of 6-chloro-2-methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine (II) as a solid, m.p. 160-169°. Recrystallization from dilute ethanol gave pale yellow needles, m.p. 174-175°, the ir spectrum of which was identical with that of an authentic sample (3).

The above insoluble material gave 4.1 g. (35.4%) of 1-[2-methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine-6-yl]pyridinium *N*,*N*-betaine (IV), m.p. 236° dec., which was recrystallized from 78% aqueous ethanol to give yellow prisms, m.p. 240° dec., ir (potassium bromide) 1355, 1365 (SO_2).

Anal. Calcd. for $C_{16}H_{13}N_5O_5S$ (mol. wt. = 387.30); C, 49.62; H, 3.38; N, 18.08. Found: C, 49.72; H, 3.63; N, 18.07.

The aqueous filtrate obtained above was then concentrated under reduced pressure and the residue was treated with 8 ml. of water. The crystals which separated were collected to give 2 g. (19.5%) of *N*-(*p*-nitrobenzenesulfonyl)-β-ureido-β-pyridiniumacrylamide *N*,*N*-betaine (V), m.p. 230° dec., which was recrystallized from water to give pale yellow needles, m.p. 243-245°.

Anal. Calcd. for $C_{15}H_{13}N_5O_6S{\cdot}H_2O$: C, 44.01; H, 3.69; N, 17.11. Found: C, 44.20; H, 3.33; N, 17.06.

This hydrate was dried *in vacuo* over phosphorous pentoxide at 70-80° to give the anhydrous compound.

Anal. Calcd. for $C_{15}H_{13}N_5O_6S$: C, 46.06; H, 3.35; N, 17.90. Found: C, 45.88; H, 3.28; N, 17.58.

1-[2-Methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine-6-yl]pyridinium *N*,*N*-Betaine (IV).

A solution of 0.3 g. (0.87 mmole) of III in 2 ml. of dry pyridine was heated at 95° for 30 minutes. The reaction mixture was cooled and allowed to stand whereupon crystals separated. The crystals were collected by filtration, washed with water and recrystallized from 70% aqueous ethanol to give 0.32 g. (95.0%) of IV as yellow prisms, m.p. 240° dec., which was identical with the authentic sample.

1-[2-Methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine-6-yl]pyridinium Chloride Hydrochloride (VI).

A solution of 387 mg. (1 mmole) of IV in 10% aqueous hydrochloric acid solution was decolorlized by treatment with active charcoal at 70-80° and filtered while hot. The filtrate was cooled and allowed to stand whereupon crystals separated which were collected by filtration to give 350 mg. (76.1%) of VI as colorless needles, m.p. 270° dec. This compound was analyzed without recrystallization because of its instability.

Anal. Calcd. for $C_{16}H_{14}ClN_5O_5S{\cdot}HCl$: C, 41.75; H, 3.29; N, 15.21. Found: C, 42.04; H, 3.51; N, 15.10.

This compound was dissolved in water and the resulting solution was allowed to stand to separate yellow prisms, m.p. 240° dec., the ir spectrum of which was identical with that of IV.

1-[2-Methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine-6-yl]pyridinium Bromide (VII).

A solution of 387 mg. (1 mmole) of IV in 5 ml. of 20% hydrobromic acid was treated with active charcoal at 70-80°. Similar treatment of the above product as in the case of VI gave 330 mg. (70.5%) of VII as colorless prisms, m.p. 220° dec.

Anal. Calcd. for $C_{16}H_{14}BrN_5O_5S$: C, 41.04; H, 3.02; N, 14.96. Found: C, 40.79; H, 2.79; N, 14.66.

1-[2-Methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine-6-yl]pyridinium Perchlorate (VIII).

To a solution of 1 g. (2.17 mmoles) of VI in 70 ml. of hot water was added dropwise 2 ml. of 60% perchloric acid with stirring. The precipitate which separated was collected by filtration to give 0.8 g. of VIII, m.p. 203° dec., which on recrystallization from dilute methanol gave 0.65 g. (61.4%) of VIII as colorless needles, m.p. 220° dec.

Anal. Calcd. for $C_{16}H_{14}ClN_5O_9S$: C, 39.39; H, 2.89; N, 14.35. Found: C, 39.56; H, 2.96; N, 14.55.

1-[2-Methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine-6-yl]pyridinium Chloroferrate (IX).

To a solution of 387 mg. (1 mmole) of IV in 5 ml. of 20% hydrochloric acid was added dropwise 5 ml. of 50% aqueous ferric chloride hexahydrate. The yellow crystals which separated were collected by filtration, washed with a small amount of cold methanol, and recrystallized from acetic acid to give 350 mg. (59.7%) of IX as yellow prisms, m.p. 174° dec.

Anal. Calcd. for $C_{16}H_{14}Cl_4FeN_5O_5S \cdot \frac{1}{2}H_2O$ (13): C, 32.31; H, 2.54; N, 11.77. Found: C, 32.74; H, 2.43; N, 11.34.

1-[2-Methoxy-4-(*p*-nitrobenzenesulfonamide)pyrimidine-6-yl]pyridinium Iodide (X).

To a solution of 0.5 g. of potassium iodide in water was added with stirring 0.5 g. (1.08 mmoles) of VI. The yellow crystals which separated were collected by filtration, washed with water and recrystallized from methanol to give 450 mg. (80.9%) of X as yellow prisms, m.p. 285-290° dec.

Anal. Calcd. for $C_{16}H_{14}IN_5O_5S$: C, 37.29; H, 2.73; N, 13.59. Found: C, 37.47; H, 2.64; N, 13.52.

6-Amino-2-methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine (XI).

A solution of 1.15 g. (2.97 mmoles) of IV in 40 ml. of 15% (w/v) methanolic ammonia was stirred at room temperature for 48 hours in a sealed tube. The reaction mixture was filtered to remove an insoluble material and the filtrate was concentrated under reduced pressure. The residue was diluted with water and filtered to give 0.8 g. (82.8%) of XI, which on recrystallization from 50% aqueous acetone gave 7 g. (72.5%) of colorless plates, m.p. 201° dec.; nmr (5% solution in hexadeuteriodimethylsulfoxide) δ 3.82 (3H, s, OCH_3), 5.82 (1H, s, pyrimidine 5H), 7.30 (2H, s, NH_2), 8.20 (4H, q, aromatic H) and 12.5 (1H, broad, $NHSO_2$).

Anal. Calcd. for $C_{11}H_{11}N_5O_5S \cdot \frac{1}{2}H_2O$ (13): C, 39.55; H, 3.61; N, 20.95. Found: C, 40.01; H, 3.77; N, 20.94.

Hydrolysis of IV.

A mixture of 0.5 g. (1.29 mmoles) of IV and 20 ml. of 10% hydrochloric acid was heated in a sealed tube at 150° for 5 hours. After cooling, the separated crystals were collected by filtration and recrystallized from water to give 0.25 g. (96.2%) of *p*-nitrobenzenesulfonamide as colorless prisms, m.p. 178° [lit. (14) 178-190°].

Anal. Calcd. for $C_6H_6N_2O_4S$: C, 35.65; H, 2.99; N, 13.86. Found: C, 35.45; H, 3.10; N, 13.88.

The above filtrate was concentrated under reduced pressure. The separated crystals were collected by filtration to give ammonium chloride as colorless prisms, m.p. $> 350°$. Moreover, pyridine was detected, when the filtrate was basified with 10% aqueous sodium hydroxide solution.

4-Benzenesulfonamido-6-chloro-2-methoxypyrimidine (XII).

A solution of 3.2 g. (0.02 mole) of I and 3.6 g. (0.02 mole) of benzenesulfonyl chloride in 5 ml. of dry pyridine was allowed to stand at room temperature overnight and poured into 50 ml. of water. The separated crystals were collected by filtration and recrystallization from dilute methanol to give 5.2 g. (86.8%) of XII as colorless needles, m.p. 138°.

Anal. Calcd. for $C_{11}H_{10}ClN_3O_3S$: C, 44.07; H, 3.32; N, 14.01. Found: C, 43.78; H, 3.32; N, 13.98.

N-[2-Methoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine-6-yl]trimethylammonium *N,N*-Betaine (XIII).

To a solution of 4.8 g. (0.03 mole) of I in 20 ml. of benzene containing 4 g. of trimethylamine was added dropwise a solution of 6.7 g. (0.03 mole) of II in 20 ml. of dichloromethane and 5 ml. of benzene at 3-5° with stirring during 1 hour and the stirring was continued at below 5° for 5 hours. The reaction mixture was concentrated under reduced pressure at below 30° and the residue was diluted with water. The insoluble material was collected by filtration and recrystallized from methanol to give 4.4 g. (40%) of XIII as pale yellow granules, m.p. 218° dec.; ir (potassium bromide) 1615 (pyrimidine CH=N), 1530 (NO_2), 1360 and 1145 (SO_2).

Anal. Calcd. for $C_{14}H_{17}N_5O_5S$: C, 45.77; H, 4.67; N, 19.07. Found: C, 45.56; H, 4.45; N, 18.88.

6-Chloro-2-methoxy-4-(*p*-nitrobenzamido)pyrimidine (XIV).

A mixture of 3.2 g. (0.02 mole) of I and 3.8 g. (0.02 mole) of *p*-nitrobenzoyl chloride was treated with 4 ml. of dry pyridine to give a solid, which was diluted with 30 ml. of water and filtered to afford 5.6 g. (90.8%) of XIV. This was recrystallized from methanol to give colorless needles, m.p. 224°; ir (potassium bromide) 3400 (NH), 1700 (CO), 1575 (pyrimidine CH=N) and 1520 (NO_2).

Anal. Calcd. for $C_{12}H_9ClN_4O_4$: C, 46.69; H, 2.93; N, 18.15. Found: C, 46.84; H, 3.02; N, 18.42.

1-[2-Ethoxy-4-(*p*-nitrobenzenesulfonamido)pyrimidine-6-yl]pyridinium *N,N*-Betaine (XVI).

A solution of 3.47 g. (0.02 mole) of XV and 4.5 g. (0.02 mole) of II in 5 ml. of dry pyridine was allowed to stand at room temperature for 40 hours. The reaction mixture was poured into 80 ml. of water and allowed to stand overnight. The crystals which separated were collected by filtration, washed with 80 ml. of hot ethanol and dried to give 3 g. (37.4%) of XVI, which on recrystallization from 70% aqueous ethanol gave yellow needles, m.p. 216° dec., ir (potassium bromide) 1610 (pyrimidine CH=N), 1515 (NO_2), 1355, 1345, and 1140 (SO_2).

Anal. Calcd. for $C_{17}H_{15}N_5O_5S \cdot \frac{1}{2}H_2O$ (13): C, 49.75; H, 3.93; N, 17.06. Found: C, 49.89; H, 3.98; N, 17.32.

N-(*p*-Nitrobenzenesulfonyl)-β-ureido-β-pyridiniumacrylamide *N,N*-Betaine (V).

To a solution of 3.0 g. (10 mmoles) of *p*-nitrobenzenesulfonylpyridinium chloride in 30 ml. of chloroform and 3 ml. of methanol was added 1.6 g. (10 mmoles) of 4-amino-6-chloropyrimidine (I). The resulting mixture was refluxed for 10 hours. The solvent was removed under reduced pressure and the residue was diluted with a small amount of water and filtered to give 0.8 g. (19.6%) of V, m.p. 235° dec., which on recrystallization from dilute ethanol gave pale yellow needles, m.p. 243-245° dec., identical with the above sample by the mixed melting point test and infrared spectral comparison.

The Molecular Determination of IV by X-ray Analysis.

From Weissenberg (*h0l-h2l*) and precession (*hk0, hkl*) photographs, taken with CuKα radiation, lattice parameters and space group were determined. Density measurement was carried out by the flotation method in a mixture of chloroform and carbon tetrachloride.

Treatment of V with Sodium Nitrite in Hydrochloric Acid.

To a stirred solution of 1 g. (2.5 mmoles) of V in 35 ml. of 10% hydrochloric acid was added dropwise a solution of 400 mg. (5 mmoles) of sodium nitrite in 4 ml. of water during 15 minutes at 10° and the stirring was continued for 2 hours at 20°. After the evolution of nitrogen and carbon dioxide had ceased, the resulting orange solution was evaporated under reduced pressure and the residue was triturated with 20 ml. of ethanol and filtered to remove sodium chloride. The filtrate was evaporated and the residue was dissolved in 1 ml. of hot water. This was allowed to stand in a refrigerator to separate 120 mg. of *p*-nitrobenzenesulfonamide, m.p. 175°, identical with the sample prepared by Baker (14). On the other hand, pyridine was detected when the above aqueous filtrate was basified with aqueous sodium hydroxide solution.

Acknowledgement.

We are grateful to President K. Ueno and Director H. Sano of the Chugai Pharmaceutical Co. Ltd., for their encouragement. We also thank Dr. Y. Imai for his helpful discussion and encouragement.

REFERENCES

(1) Presented at the Tohoku Branch Meeting of the Pharmaceutical Society of Japan, February, 1970.

(2) Part IV, K. Okui, K. Ito, and T. Kametani, *J. Heterocyclic Chem.*, 9, 821 (1972).

(3) Communication concerning this paper should be directed to Professor Tetsuji Kametani.

(4) Th. Zincke, *Ann. Chem.*, 333, 296 (1904).
(5) W. Klotzer, *Monatsh. Chem.*, 87, 313 (1956).
(6) G. C. Barett, V. V. Kane, and G. Lowe, *J. Chem. Soc.*, 783 (1964).
(7) L. C. King, *J. Am. Chem. Soc.*, **66**, 894 (1944).
(8) A. H. Blatt and N. Gross, *ibid.*, 77, 5424 (1955).
(9) T. Uno, K. Machida, and K. Hanai, *Spectrochim. Acta*, 22, 2065 (1966).
(10) Idem., *ibid.*, **24**, 1705 (1968).
(11) A. A. Santilli and D. H. Kim. U. S. Patent 3,452,018; *Chem. Abstr.*, 71, 61413 (1969).

(12) All melting points were determined on Yanagimoto Micro Melting point apparatus and are uncorrected. Infrared spectra were measured with a Hitachi EPI 2 spectrophotometer and partly with a Hitachi grating ir spectrophotometer Model EPI-G3, and nmr spectra were taken with a Hitachi Perkin-Elmer R-20A spectrometer using tetramethylsilane as an internal standard.

(13) These compounds were dried over phosphorus pentoxide at 80-90° for 10 hours.

(14) R. H. Baker, R. M. Dodson, and B. Reigel, *J. Am. Chem. Soc.*, 68, 2636 (1946).