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Pyrimidine and Fused Pyrimidine Derivatives. III.[1] Synthesis of *s*-Triazolo[1,5-*a*]pyrimidine Derivatives by Using Ketene Dithioacetals

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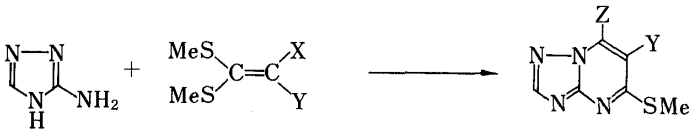
The reaction of 3-amino-*s*-triazole (**1**) with ketene dithioacetals (**2**) gave 5-methylthio-*s*-triazolo[1,5-*a*]pyrimidine derivatives in satisfactory yields. The synthesis of 7-amino-*s*-triazolo-[1,5-*a*]pyrimidine derivatives is also described.

Keywords——*s*-triazolo[1,5-*a*]pyrimidine; 3-amino-1*H*-*s*-triazole; ketene dithioacetal; displacement; aminolysis

Triazolo[1,5-*a*]pyrimidines are of considerable chemical and pharmacological importance. In particular, trypamine, 7-(*N*,*N*-diethylamino)-5-methyl-*s*-triazolo[1,5-*a*]pyrimidine, synthesized by Tenor and Ludwig,[2] is used clinically as a coronary dilator. Thus, we were interested in preparing functionalized triazolo[1,5-*a*]pyrimidines for study as potential cardiovascular agents.

Appropriately functionalized (cyano, ester carbonyl, ketone carbonyl, sulfonyl, pyridinium, *etc.*) ketene dithioacetals are very useful reagents for the synthesis of heterocyclic compounds.[1] It has been reported that the reaction of 2-aminopyridine with ketene dithioacetals gave cyclized products, 4-oxo-4*H*-pyrido[1,2-*a*]pyrimidine derivatives.[3] We applied the above reaction to the preparation of the title compounds.

Reaction of 3-amino-1*H*-*s*-triazole (**1a**) with bis(methylthio)methylenemalononitrile (**2a**)[4] at 150 °C for 1.5 h gave 7-amino-6-cyano-5-methylthio-*s*-triazolo[1,5-*a*]pyrimidine (**3**) in 70% yield. Similarly, the reaction of **1** with bis(methylthio)methylenephenylsulfonylacetonitrile (**2b**)[5] or bis(methylthio)methylenemethylsulfonylacetonitrile (**2c**)[5,6] gave 7-amino-5-methylthio-*s*-triazolo[1,5-*a*]pyrimidines (**4** and **5**) in 76 and 73% yields, respectively. 7-Aryl derivatives, 5-methylthio-7-phenyl-*s*-triazolo[1,5-*a*]pyrimidines (**6** and **7**), were prepared by the reaction of **1** with the corresponding ketene dithioacetals (**2d**, bis(methylthio)methylenecyanoacetophenone;[7] **2e**, bis(methylthio)methyleneacetophenone)[8] under the same conditions as used for the synthsis of **3** or **4**. When a mixture of **1** and methyl bis(methylthio)-methylenecyanoacetate (**2f**)[4] was heated at 150 °C for 1.5 h, the expected compound, 6-cyano-7-hydroxy-5-methylthio-*s*-triazolo[1,5-*a*]pyrimidine (**8**), was obtained in 32% yield. The above reaction was also carried out using potassium carbonate as a base in *N*,*N*-dimethylformamide (DMF) to give the desired compound (**8**) in 83% yield. Dimethyl bis-(methylthio)methylenemalonate (**2g**)[4] was reacted with **1** in the presence of potassium carbonate to give 7-hydroxy-6-methoxycarbonyl-5-methylthio-*s*-triazolo[1,5-*a*]pyrimidine (**9**) in 57% yield. Similarly, 5-methylthio-6-oxo-6*H*-indeno[2,1-*e*]-*s*-triazolo[1,5-*a*]pyrimidine (**10**) was also prepared by the condensation of **1** with 2-bis(methylthio)methylene-1,3-indandione (**2h**)[9] in 85% yield.



1 2a–h 3–10

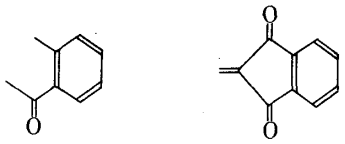
No.	products Y	Z	X	ketene dithioacetals Y		reaction conditions	yield (%)
3:	CN	NH_2	CN	CN	(2a)	150 °C 1.5 h	70
4:	SO_2–Ph	NH_2	CN	SO_2–Ph	(2b)	150 °C 1.5 h	76
5:	SO_2–Me	NH_2	CN	SO_2–Me	(2c)	150 °C 1.5 h	73
6:	CN	Ph	COPh	CN	(2d)	100 °C 2 h	87
7:	H	Ph	COPh	H	(2e)	150 °C 3 h	55
8:	CN	OH	COOMe	CN	(2f)	150 °C 2 h	32
						K_2CO_3 3 h	83
9:	COOMe	OH	COOMe	COOMe	(2g)	K_2CO_3 3 h	57
10:					(2h)	K_2CO_3 3 h	85

Chart 1

We attempted the preparation of 5-amino derivatives by displacement of the methylthio group at the 5-position of **8** and **10**. It was found that the methylthio group on the fused pyrimidine ring could be displaced with nucleophiles such as amines or active methylene compounds.[10] Compound **8** was allowed to react with amines (ammonia, aniline, *p*-chloroaniline, 2,2-dimethoxyethylamine, diethylamine, morpholine, and *N*-methylpiperazine) to give the corresponding 5-amino-6-cyano-7-hydroxy-*s*-triazolo[1,5-*a*]pyrimidines (**11a—g**) in good yields. The reaction of **10** with amines (piperidine and morpholine) also gave the corresponding 5-amino derivatives (**12a, b**).

Trypamine has an *N*,*N*-diethylamino group at the 7-position of *s*-triazolo[1,5-*a*]pyrimidine. Thus, we tried to synthesize various 7-amino derivatives. The key intermediates for 7-amino-*s*-triazolo[1,5-*a*]pyrimidines are the corresponding 7-chloro derivatives (**13—16**), which were prepared by chlorination of **8**, **11b**, **11c**, and **11f** with phosphorus oxychloride. When **8** was allowed to react with phosphorus oxychloride in the presence of *N*,*N*-dimethylaniline, two products, 7-(*p*-*N*,*N*-dimethylamino)phenyl-6-cyano-5-methylthio-*s*-triazolo[1,5-*a*]pyrimidine (**18**) and 7-chloro-5-(*p*-*N*,*N*-dimethylamino)phenyl-6-cyano-*s*-triazolo[1,5-*a*]pyrimidine (**17**) were obtained in a ratio of 1 : 1. The structure of **17** was evident from the spectral (see Experimental) and chemical data. Treatment of **17** with ammonia in ethanol gave 7-amino-6-cyano-5-(*p*-*N*,*N*-dimethylamino)phenyl-*s*-triazolo[1,5-*a*]pyrimidine (**20a**), which was identical with a sample prepared by the reaction of **1** with 2-cyano-3-(*p*-*N*,*N*-dimethylamino)phenyl-3-methylthioacrylonitrile (**19**). Other amino derivatives (**b—d**) were obtained by aminolysis of **17** with amines (aniline, piperidine, and morpholine). The reaction of **13** with amines (aniline, morpholine, and *N*-methylpiperazine) gave the corresponding 5,7-diamino-6-cyano-*s*-triazolo[1,5-*a*]pyrimidines (**21a—c**). Other 5,7-diamino-6-cyano-*s*-triazolo[1,5-*a*]pyrimidine derivatives (**22a, b**) were prepared by the aminolysis of 5-(substituted amino)-6-cyano-7-chloro-*s*-triazolo[1,5-*a*]pyrimidines (**14** and **16**).

Experimental

All melting points were determined in a capillary tube and are uncorrected. Infrared (IR) spectra were recorded

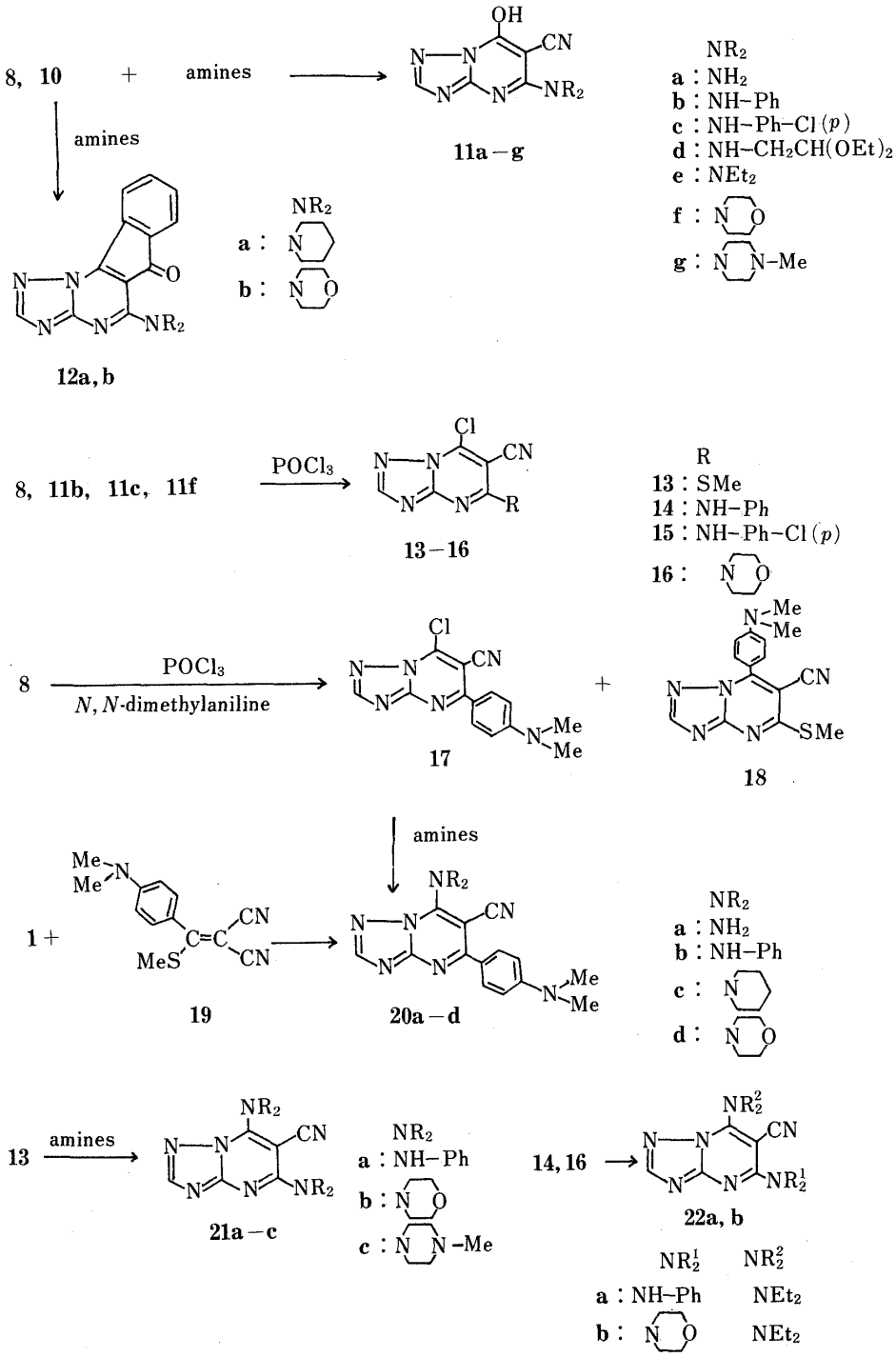
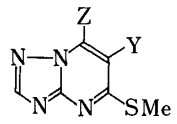


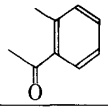
Chart 2

in KBr pellets on a JASCO IRA-2 spectrometer, ultraviolet (UV) absorption spectra were determined in 95% EtOH on a Hitachi EPS2 spectrometer, and nuclear magnetic resonance (NMR) spectra were obtained on JNM-PS-100 (100 MHz) and JNM-PMX-60 (60 MHz) spectrometers with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on a JEOL JMS-01SG mass spectrometer.

Condensation of 3-Amino-1*H*-*s*-triazole (1) with Ketene Dithioacetals——a) A mixture of **1** (10 mmol) and a ketene dithioacetal (**2a—f**) (10 mmol) was heated at 100—150 °C for 1.5—3 h. The product was recrystallized from a suitable solvent (Table I) to give the pure crystals in 32—87% yields. In the case of the reaction of **1** with **2f**, the reaction mixture was dissolved in 10% NaOH solution and then acidified with 10% HCl. The yellow solid that appeared was collected by suction and recrystallized from MeOH–C_6H_6 to give yellow needles, mp 270 °C, in 32% yield. b) A mixture of **1** (10 mmol), a ketene dithioacetal (**2f—h**) (10 mmol), and DMF (30 ml) was heated at 150 °C on

TABLE I. 6,7-Disubstituted 5-Methylthio-*s*-triazolo[1,5-*a*]pyrimidine Derivatives



No.	Y	Z	Yield (%)	mp (°C)	Recryst. solvent	Appearance	Formula	Analysis (%) Calcd (Found)			
								C	H	N	S
3	CN	NH_2	70	318	MeOH–C_6H_6	Pale yellow needles	$C_7H_6N_6S$	40.77 (40.59)	2.93 2.90	40.75 40.82	15.55 15.37)
4	SO_2–Ph	NH_2	94	279	MeOH–C_6H_6	Colorless needles	$C_7H_{11}N_5O_2S_2$	44.85 (44.66)	3.45 3.36	21.79 21.77	19.95 19.60)
5	SO_2–Me	NH_2	92	306	MeOH–C_6H_6	Colorless needles	$C_7H_9N_5O_2S_2$	32.42 (32.28)	3.50 3.50	27.01 26.83	24.73 24.47)
6	CN	Ph	87	195	MeOH	Colorless needles	$C_{13}H_9N_5S$	58.41 (58.43)	3.39 3.34	26.20 26.30	11.99 12.06)
7	H	Ph	55	168	MeOH	Colorless needles	$C_{12}H_{10}N_4S$	59.48 (59.12)	4.16 4.12	23.12 23.31	13.33 12.92)
8	CN	OH	32 83	270	MeOH–C_6H_6	Yellow needles	$C_7H_5N_5OS$	40.58 (40.49)	2.43 2.39	33.80 34.07	15.47 15.54)
9	COOMe	OH	57	220	AcOH	Tan needles	$C_8H_8N_4O_3S$	40.00 (39.83)	3.36 3.29	23.32 23.25	13.35 13.41)
10			85	312	MeOH–C_6H_6	Yellow needles	$C_{13}H_8N_4OS$	58.20 (57.97)	3.01 3.04	20.88 20.95	11.95 11.78)

No.	MS m/e (M^+)	IR ν(KBr) cm^{-1}	UV λ_{max}^{EtOH} nm (log ε)	NMR δ (ppm)
3	206	2200 (CN)	255 (4.65), 260 (4.65) 290 (3.96), 302 (3.81)	T 2.80 (3H, s, SMe), 7.86 (2H, br s, NH_2), 8.77 (1H, s, 2-H)
4	321	3350 (NH) 3100 (NH)	268[a]	D 2.40 (3H, s, SMe), 7.48—7.78 (3H, m, phenyl-H), 7.97—8.09 (2H, m, phenyl-H), 8.94 (2H, br s, NH_2), 9.35 (1H, s, 2-H)
5	259	3340 (NH) 3080 (NH)	264[a]	D 2.51 (3H, s, SMe), 3.32 (3H, s, SO_2–Me), 8.47 (2H, br s, NH_2), 9.32 (1H, s, 2-H)
6	267	2200 (CN)	228 (4.16), 254 (4.28) 274 (4.42), 310 (3.98)	D 2.74 (3H, s, SMe), 7.63—7.95 (5H, m, phenyl-H), 8.62 (1H, s, 2-H)
7	242		256 (4.34), 307 (4.21)	C 2.73 (3H, s, SMe), 7.01 (1H, s, 6-H), 7.54—7.65 (3H, m, phenyl-H), 7.95—8.06 (2H, m, phenyl-H), 8.37 (1H, s, 2-H)
8	207	2200 (CN) 1618 (CO)	220,[a] 310[a]	T 3.20 (3H, s, SMe), 8.59 (1H, s, 2-H)
9	240	3140—2300 (wide, OH) 1720 (CO) 1650 (CO)	220 (4.21), 226 (4.21) 292 (3.83)	T 3.08 (3H, s, SMe), 4.20 (3H, s, OMe), 8.90 (1H, s, 2-H)
10	268	1710 (CO)	230 (4.43), 260 (4.43) 267 (4.46), 286 (4.55) 292 (4.61), 390 (3.35)	C 2.75 (3H, s, SMe), 7.62—7.87 (3H, m, aromatic-H), 8.25—8.39 (1H, m, 7-H)

a) Insufficient solubility. T, CF_3COOH; D, DMSO-d_6; C, $CDCl_3$.

an oil bath for 3 h. The reaction mixture was then poured into 200 ml of water and acidified with 10% HCl. The precipitates that appeared were collected by suction and recrystallized from a suitable solvent (Table I).

5-Amino-6-cyano-7-hydroxy-*s*-triazolo[1,5-*a*]pyrimidine (11a)——A solution of **8** (0.62 g, 3 mmol) and 10 ml of 28% ammonia in 15 ml of EtOH was refluxed for 1 h, followed by removal of the EtOH and excess ammonia. The

TABLE II. 5-(Substituted Amino)-6-cyano-7-hydroxy-*s*-triazolo[1,5-*a*]pyrimidines

No.	NR_2	Yield (%)	mp (°C)	Recryst. solvent	Appearance	Formula	Analysis (%) Calcd (Found) C	H	N	IR ν (KBr) cm^{-1}	UV λ_{max}^{EtOH} (log ε)
11a	NH_2	61	>360	AcOH	White needles	$C_6H_4N_6O$	40.91 (41.05	2.29 2.32	47.72 47.43)	2230 (CN) 1610 (CO) 3120, 3330 (NH)	227,[a] 263, 273
11b	NH–Ph	40	324	AcOH	White crystals	$C_{12}H_8N_6O$	57.14 (57.02	3.20 3.17	33.32 32.97)	2200 (CN) 1650 (CO) 3290 (NH)	230 (4.49), 278 (4.05)
11c	NH–Ph–Cl(*p*)	98	327	AcOH	White needles	$C_{12}H_7ClN_6O$	48.49 (48.37	3.20 3.17	24.24 24.36)	2200 (CN) 1640 (CO) 3120, 3320 (NH)	279 (4.38), 233 (4.35), 320 (3.99)
11d	$NH-CH_2CH(OEt)_2$	30	198	EtOH	White crystals	$C_{12}H_{16}N_6O_3$	49.31 (49.57	5.52 5.33	28.75 28.53)	2200 (CN) 1632 (CO) 3300 (NH)	230 (4.46), 272 (4.07)
11e	NEt_2	34	223	EtOH	White plates	$C_{10}H_{12}N_6O$	51.72 (51.67	5.21 5.10	36.19 36.28)	2210 (CN) 1650 (CO) 3100 (NH)	220 (4.32), 256 (3.93)
11f		48	315	AcOH	White crystals	$C_{10}H_{10}N_6O_2$	48.74 (48.88	4.09 4.15	34.13 34.13)	2200 (CN) 1675 (CO) 3100 (NH)	230 (4.44), 295 (4.11)
11g		45	280	MeOH–C_6H_6	White crystals	$C_{11}H_{13}N_7O$	50.96 (50.20	5.05 5.11	37.82 37.33)	2200 (CN) 1625 (CO) 3100 (NH)	230,[a] 297

a) Insufficient solubility.

TABLE III. 5-Substituted 7-Chloro-6-cyano-*s*-triazolo[1,5-*a*]pyrimidines

No.	R^1	R^2	Yield (%)	mp (°C)	Appearance	Formula	Analysis (%) Calcd (Found) C	H	N	S	IR ν (KBr) cm^{-1}	UV λ_{max}^{EtOH} (log ε)
13	SMe	CN	95	130	Pale yellow leaflets	$C_7H_4ClN_5S$	37.26 (37.31	1.79 1.72	31.04 31.12	14.21 14.35)	2200 (CN)	220 (4.27) 242 (4.17) 258 (3.91) 298 (4.00) 304 (3.99)
14	NH–Ph	CN	91	302	Colorless powder	$C_{12}H_7ClN_6$	53.25 (53.16	2.61 2.64	31.05 31.10)		2200 (CN) 3260 (NH)	220 (4.46) 284 (4.09) 298 (4.12)
15	NH–Ph–Cl(*p*)	CN	70	251	Colorless needles	$C_{12}H_6Cl_2N_6$	44.60 (44.71	2.50 2.37	26.01 26.22)		2200 (CN) 3400 (NH)	220 (4.36) 281 (4.12) 318 (4.09)
16		CN	93	166	Yellow needles	$C_{10}H_9ClN_6O$	45.38 (45.38	3.43 3.44	31.75 31.96)		2200 (CN)	222 (4.40) 236 (4.30) 312 (4.19)

residue was recrystallized from AcOH to give 0.32 g (61%) of colorless needles, mp 360 °C (see Table II).

5-(Substituted Amino)-6-cyano-7-hydroxy-*s*-triazolo[1,5-*a*]pyrimidines (11b—g)——A mixture of **8** (10 mmol) and an amine (aniline, *p*-chloroaniline, 2,2-dimethoxyethylamine, diethylamine, morpholine, or *N*-methylpiperazine) (40 ml) was heated at 120 °C for 2 h, then cooled. The product was washed with MeOH and recrystallized from MeOH–C_6H_6 to give the corresponding amino compound (**11b—g**) (see Table II).

6-Oxo-5-piperidino-6*H*-indeno[2,1-*e*]-*s*-triazolo[1,5-*a*]pyrimidine (12a)——A mixture of 1.34 g (5 mmol) of **10** and 1.7 g (20 mmol) of piperidine was heated at 150 °C for 1 h, then cooled. Then product was washed with MeOH and recrystallized from MeOH–C_6H_6 to give 1.10 g (72%) of tan needles, mp 226 °C. IR ν(KBr) cm^{-1}: 1700, 1620 (C=O). UV λ_{max}^{EtOH} nm (log ε): 219 (4.44), 256 (4.58), 264 (4.62), 300 (4.23), 412 (3.25). *Anal.* Calcd for $C_{17}H_{15}N_5O$: C, 66.87; H, 4.95; N, 22.94. Found: C, 67.18; H, 4.88; N, 23.23.

6-Oxo-5-morpholino-6*H*-indeno[2,1-*e*]-*s*-triazolo[1,5-*a*]pyrimidine (12b)——This compound was synthesized in 61% yield from **10** and morpholine in a manner similar to that described for the preparation of **12a**. An analytical sample was recrystallized from MeOH–C_6H_6 to give tan needles, mp 282 °C. IR ν(KBr) cm^{-1}: 1692, 1623 (C=O). UV λ_{max}^{EtOH} (poorly soluble): 216, 240, 263, 298, 364; λ_{min}: 230, 346. *Anal.* Calcd for $C_{16}H_{13}N_5O_2$: C, 62.53; H, 4.26; N, 22.79. Found: C, 62.69; H, 4.27; N, 22.95.

5-Substituted 7-Chloro-6-cyano-*s*-triazolo[1,5-*a*]pyrimidine Derivatives (13—16)——A suspension of a 7-hydroxy compound (**8**, **11b**, **11c**, or **11f**) in $POCl_3$ (ten-fold excess) was heated at 100 °C for 2 h. After evaporation of excess $POCl_3$ under reduced pressure, the residue was poured into ice-water. The mixture was neutralized with K_2CO_3 solution. The precipitate was collected by suction and recrystallized from benzene to give the corresponding 7-chloro derivative (**13—16**) (see Table III).

Treatment of 8 with $POCl_3$ in the Presence of *N*,*N*-Dimethylaniline——A mixture of 4.1 g (20 mmol) of **8**, 50 ml of $POCl_3$, and 9 ml of *N*,*N*-dimethylaniline was refluxed for 2.5 h. After evaporation of excess $POCl_3$ under reduced pressure, the residue was poured into ice-water. The precipitate was collected by filtration. The product was a mixture of **17** and **18**. The NMR spectrum ($CDCl_3$ δ) showed two singlets (1 : 1) at 8.47 and 8.60 ppm due to protons at the 2-position of **17** and **18**. The product was recrystallized from MeOH to give 2.11 g (38%) of **17** as colorless needles, mp 294 °C. IR ν(KBr) cm^{-1}: 2200 (CN). UV λ_{max}^{EtOH} nm (log ε): 227 (4.28), 248 (4.33), 265 (4.37), 310 (3.61), 422 (4.41). NMR ($CDCl_3$) δ: 3.14 (6H, s, N-Me), 6.86 (2H, d, J=9.5 Hz, 3′-H, 5′-H), 8.18 (2H, d, J=9.5 Hz, 2′-H, 6′-H), 8.62 (1H, s, 2-H). MS: *m/e* 298, 300 (M^+). *Anal.* Calcd for $C_{14}H_{11}ClN_6$: C, 56.29; H, 3.71; N, 28.13. Found: C, 56.14; H, 3.60; N, 28.26.

The mother liquor was evaporated under reduced pressure and the residue was chromatographed on a neutral alumina column using benzene–$CHCl_3$ (2 : 1) as the eluent to give 1.86 g (30%) of **18** as a yellow powder, mp 360 °C. IR ν(KBr) cm^{-1}: 2200 (CN). UV λ_{max}^{EtOH} nm (log ε): 227 (4.28), 248 (4.33), 265 (4.37), 310 (3.61), 422 (4.41). NMR ($CDCl_3$) δ: 2.72 (3H, s, SMe), 3.10 (6H, s, N-Me), 6.84 (2H, d, J=9.5 Hz, 3′-H, 5′-H), 8.06 (2H, d, J=9.5 Hz, 2′-H, 6′-H), 8.45 (1H, s, 2-H). MS: *m/e* 310 (M^+), 309 (M^+-1). *Anal.* Calcd for $C_{15}H_{14}N_6S$: C, 58.05; H, 4.55; N, 27.08; S, 10.33. Found: C, 58.03; H, 4.28; N, 27.05; S, 10.53.

7-Amino-6-cyano-5-*p*-*N*,*N*-dimethylaminophenyl-*s*-triazolo[1,5-*a*]pyrimidine (20a)——a) A mixture of 1.50 g (5 mmol) of **17** and 20 ml of saturated ammonia–MeOH was stirred at room temperature for 1 h and then refluxed for 1 h. After evaporation of the solvent and excess ammonia, the residue was recrystallized from MeOH–C_6H_6 to give 0.88 g (63%) of **20a** as yellow needles, mp 174 °C. b) A mixture of 0.84 g (10 mmol) of **1** and 2.43 g (10 mmol) of 3-(*p*-*N*,*N*-dimethylamino)phenyl-3-methylthioacrylonitrile (**19**) was heated at 150 °C for 1 h, then cooled. The product was recrystallized from MeOH–C_6H_6 to give 2.62 g (94%) of **20a** as yellow needles, mp 174 °C (see Table IV).

7-(Substituted Amino)-6-cyano-5-*p*-*N*,*N*-dimethylaminophenyl-*s*-triazolo[1,5-*a*]pyrimidines (20b—d)——A mixture of 10 mmol of **17** and 20 mmol of an amine (aniline, piperidine, or morpholine) was heated at 100 °C for 2 h, then cooled. The product was washed with water and recrystallized from MeOH to give the corresponding 7-amino derivative (**20b—d**).

3-(*p*-*N*,*N*-Dimethylamino)phenyl-3-methylthioacrylonitrile (19)——Malononitrile (1 g, 15 mmol) was added to a suspension of sodium hydride (50%, 0.72 g, 15 mmol) in 50 ml of absolute tetrahydrofuran (THF) and the mixture was stirred for 30 min at room temperature. Methyl *p*-*N*,*N*-dimethylaminophenyldithiocarboxylate (1.91 g, 10 mmol) was added to the above mixture. The whole was stirred for 1 h and then refluxed for 2 h. After evaporation of the THF, the residue was dissolved in 100 ml of water. Dimethyl sulfate (1.89 g, 15 mmol) was added dropwise to the solution and the mixture was stirred for 2 h at room temperature. The precipitate that appeared was collected by filtration and recrystallized from MeOH to give 1.50 g (62%) of yellow needles, mp 116 °C. IR ν(KBr) cm^{-1}: 2180 (CN). UV λ_{max}^{EtOH} nm (log ε): 258 (3.99), 324 (3.95), 430 (4.30). NMR ($CDCl_3$) δ: 2.38 (3H, s, SMe), 3.09 (6H, s, NMe_2), 6.73 (2H, d, J=8.8 Hz, aromatic-H), 7.45 (2H, d, J=8.8 Hz, aromatic-H). MS *m/e*: 243 (M^+). *Anal.* Calcd for $C_{13}H_{13}N_3S$: C, 64.17; H, 5.39; N, 17.27; S, 13.18. Found: C, 64.07; H, 5.40; N, 17.18; S, 13.01.

5,7-Diamino-6-cyano-*s*-triazolo[1,5-*a*]pyrimidine (21a—c)——A mixture of 10 mmol of **13** and 40 mmol of an amine (aniline, morpholine, or *N*-methylpiperazine) was heated at 100 °C for 3 h, and cooled. The product was washed with water and recrystallized from MeOH to give the corresponding 5,7-diamino derivative (**21a—c**).

7-Anilino-6-cyano-5-*N*,*N*-diethylamino-*s*-triazolo[1,5-*a*]pyrimidine (22a)——Compound **22b** was synthesized from **14** and *N*,*N*-diethylamine in a manner similar to that described for the preparation of **20b**. An analytical sample

TABLE IV. 7-Amino-6-cyano-5-*p*-*N*,*N*-dimethylaminophenyl-*s*-triazolo[1,5-*a*]pyrimidines

No.	NR_2	Yield (%)	mp (°C)	Recryst. solvent	Appearance	Formula	Analysis (%) Calcd (Found) C	H	N	IR ν (KBr) cm^{-1}	UV λ_{max}^{EtOH} (log ε)
20a	NH_2	92	299	MeOH	Yellow needles	$C_{14}H_{13}N_7$	60.20 (60.38	4.96 4.61	35.10 35.17)	2200 (CN) 3100, 3460 (NH)	245 (4.53), 264 (4.17), 318 (3.56), 400 (4.37)
20b	NH–Ph	50	272	MeOH–C_6H_6	Yellow needles	$C_{21}H_{17}N_7$	67.59 (67.97	4.82 4.78	27.59 27.31)	2200 (CN)	224,[a] 230, 270, 406
20c	N⟨ ⟩	60	185	MeOH	Yellow needles	$C_{19}H_{21}N_7$	65.69 (65.69	6.09 6.08	28.22 28.49)	2200 (CN)	216 (4.26), 264 (4.56), 404 (4.45)
20d	N⟨ O ⟩	64	242	MeOH	Yellow needles	$C_{18}H_{19}N_7O$	61.88 (61.90	5.48 5.46	28.06 27.96)	2210 (CN)	217 (4.22), 262 (4.51), 408 (4.44)

a) Insufficient solubility.

TABLE V. 5.7-Diamino-6-cyano-*s*-triazolo[1,5-*a*]pyrimidine Derivatives

No.	R^1	R^2	Yield (%)	mp (°C)	Appearance	Formula	Analysis (%) Calcd (Found) C	H	N	IR ν (KBr) cm^{-1}	UV λ_{max}^{EtOH} nm (log ε)
21a	NH–Ph	NH–Ph	37	248	Colorless needles	$C_{18}H_{13}N_7$	66.04 (66.31	4.00 3.91	29.95 30.06)	2200 (CN) 3390 (NH)	274[a]
21b	N⟨ O ⟩	N⟨ O ⟩	68	245	Colorless powder	$C_{14}H_{17}N_7O_2$	53.33 (53.21	5.43 5.48	31.09 30.95)	2200 (CN)	237 (4.30), 268 (4.71), 300 (4.27)
21c	N⟨ N–Me ⟩	N⟨ N–Me ⟩	58	187	Pale yellow needles	$C_{16}H_{23}N_9$	56.29 (55.89	6.79 6.56	36.92 37.05)	2200 (CN)	230 (4.19), 267 (4.60), 298 (4.14)
22a	NH–Ph	NEt_2	43	176	Colorless powder	$C_{16}H_{17}N_7$	62.53 (62.44	5.57 5.56	31.54 31.92)	2200 (CN) 3200 (NH)	247 (4.37), 262 (4.51), 294 (4.01)
22b	N⟨ O ⟩	NEt_2	37	174	Colorless powder	$C_{14}H_{19}N_7O$	55.80 (55.14	6.36 6.12	32.54 32.34)	2200 (CN)	240 (3.90), 268 (4.26), 300 (3.80)

a) Insufficient solubility.

was recrystallized from MeOH to give colorless needles.

6-Cyano-5-*N*,*N*-diethylamino-7-morpholino-*s*-triazolo[1,5-*a*]pyrimidine (22b)——Compound **22a** was also synthesized from **16** and morpholine in a manner similar to that described for the preparation of **20b**.

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