255 (3.89), 248 sh (3.85), 207 (4.20); mass spectrum, M+, *m/e* 217 (100).

Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.45; H, 5.11; N, 6.46. Found: C, 66.18; H, 5.02; N, 6.14.

In a similar fashion, **1,2-dicyano-4*H*-quinolizin-4-one** (**3**, **R = R¹ = CN**) was obtained from **1** and dicyanoacetylene on refluxing in chlorobenzene overnight. It crystallized from benzene as yellow prisms: mp 263–265° (33%); ir (KBr) 3150, 3140 (CH), 2225 (CN), 1710 (amide CO) cm⁻¹; $\lambda_{max}^{CH_3OH}$, nm (log ε), 415 (4.20), 394 (4.12), 278 (3.69), 261 (4.02), 235 (4.31), 212 (4.23); mass spectrum, M+, *m/e* 195 (45).

Anal. Calcd for $C_{11}H_5N_3O$: C, 67.65; H, 2.58; N, 21.53. Found: C, 67.69; H, 2.55; N, 21.49.

***anhydro*-2-Hydroxy-1-methyl-4-oxo-3-(tricyanoethenyl)pyrido[1,2-*a*]pyrimidinium Hydroxide** (**4**).—*anhydro*-2-Hydroxy-1-methyl-4-oxopyrido[1,2-*a*]pyrimidinium hydroxide (0.528 g, 3.0 mmol), tetracyanoethylene (0.561 g, 4.5 mmol), and chlorobenzene (750 ml) were heated under reflux for 15 hr. After removal of the dark, insoluble matter the hot filtrate was evaporated to dryness under reduced pressure. Trituration of the residue with a small amount of cold acetone caused it to crystallize, and it was recrystallized from acetone and then from acetonitrile–ether (1:1) from which it separated as yellow prisms: mp 301–302° (42%); ir (KBr) 3140, 2920 (CH), 2255 (CN), 1715, 1665 (CO) cm⁻¹; $\lambda_{max}^{CH_3OH}$, nm (log ε), 416 (3.20), 250 (3.98), 218 (4.36); mass spectrum, M+, *m/e* 277 (60).

Anal. Calcd for $C_{14}H_7N_5O_2$: C, 60.65; H, 2.54; N, 25.21. Found: C, 60.56; H, 2.39; N, 25.32.

Similarly, ***anhydro*-3-(1,2-dicarbethoxyhydrazino)-2-hydroxy-1-methyl-4-oxopyrido[1,2-*a*]pyrimidinium hydroxide** (**5**) was obtained from the mesoionic compound **1** and ethyl azodicarboxylate in refluxing chlorobenzene over 24 hr. In this case the crude residue was dissolved in acetone and purified[19] by chromatography on silica gel. It crystallized from benzene–*n*-heptane (2:1) as yellow, irregular prisms: mp 106–109° (24%); ir (KBr) 3315, 3225 (NH), 3100, 2998 (CH), 1770, 1750 (COOEt), 1720, 1640 (amide CO) cm⁻¹; $\lambda_{max}^{CH_3OH}$, nm (log ε), 340 sh (3.02), 330 (3.14), 265 (3.54), 230 (4.23); mass spectrum (70 eV) *m/e* (rel intensity), M+, 350 (1), 277 (5), 276 (10), 217 (15), 203 (10), 189 (15), 135 (20), 133 (15), 108 (15), 79 (32), 78 (100), 77 (15).

Anal. Calcd for $C_{15}H_{18}N_4O_6$: C, 51.43; H, 5.18; N, 15.99. Found: C, 52.72; H, 5.15; N, 15.72.

Registry No.—**1**, 26460-93-5; **3** (R = R¹ = $COOCH_3$), 4627-24-1; **3** (R = $COOC_2H_5$; R¹ = H), 24403-35-8; **3** (R = R¹ = CN), 26460-96-8; **4**, 26460-97-9; **5**, 26460-98-0.

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(19) This product always separated with fractional amounts of solvent of crystallization and several determinations of carbon contents gave results of this order.

1,2,4-Triazoles. XXVII. Synthesis of the Thiazolo[2,3-*c*]-*s*-triazole and the Thiazolo[3,2-*b*]-*s*-triazole Systems[1]

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2-Triazolylhydrazines underwent ring closure with aliphatic acids or ortho esters to thiazolo[2,3-*c*]-*s*-triazoles, cyanogen bromide, and carbon disulfide readily giving the corresponding 3-amino and 3-mercapto derivatives. The isomeric thiazolo[3,2-*b*]-*s*-triazole system was readily obtained from *s*-triazole-3-thiols and α-halo ketones. Spectral characteristics of these ring systems are described.

Fusion of the thiazole and the *s*-triazole nuclei can be effected in two ways, represented by thiazolo[2,3-*c*]-*s*-triazole (**2**) and thiazolo[3,2-*b*]-*s*-triazole (**4**). The only hitherto reported[2] examples of these ring systems are relatively complex. We now describe the synthesis and properties of alkyl- and aryl-substituted derivatives of both systems, as well as some amino and mercapto derivatives. Though the isomerization of *s*-triazolo[4,3-*a*]pyridines to *s*-triazolo[1,5-*a*]pyridines has been reported[3] as well as isomerizations in related [5,6] ring-fused systems,[4] no such isomerizations have been found in [5,5] ring-fused systems. Thiazolo-[2,3-*c*]-*s*-triazole (**2**) is particularly suitable for studying such isomerizations.

Cyclization of 2-thiazolylhydrazines[5] (**1**), a synthetic approach well documented for the preparation of ring-fused *s*-triazoles,[6] has provided a simple synthesis of the fused-ring system **2** (Table I). Cyclization of 4-methyl-2-thiazolylhydrazine (**1**, R = CH_3) with formic, acetic, or propionic acids under reflux for 6–8 hr led directly to **2**. However, 4-phenyl-2-thiazolylhydrazine (**1**, R = Ph) gave the intermediate hydrazides (**3**, R = Ph; R¹ = CH_3, Et) with acetic and propionic acids and these hydrazides underwent a smooth cyclization to the fused system **2** with phosphoryl chloride. Ortho esters were equally effective as cyclization agents but slightly longer reaction periods were required. Attempts to prepare the fused system **2** with 3-phenyl substituents by the cyclization of the 2-thiazolylhydrazines (**1**) with benzoic acid were unsuccessful. However, phosphoryl chloride cyclization of 2-[4-methyl(phenyl)thiazol-2-yl]benzhydrazide [**3**, R = CH_3(Ph); R¹ = Ph], prepared from 1-benzoylthiosemicarbazide and chloroacetone, or phenacyl bromide, respectively, gave **2**. The ease of these cyclizations are particularly interesting in view of the formation of 2-azidothiazole on attempted ring closure of 2-amino or 2-hydrazinothiazole to thiazolo[3,2-*d*]-tetrazole.[7]

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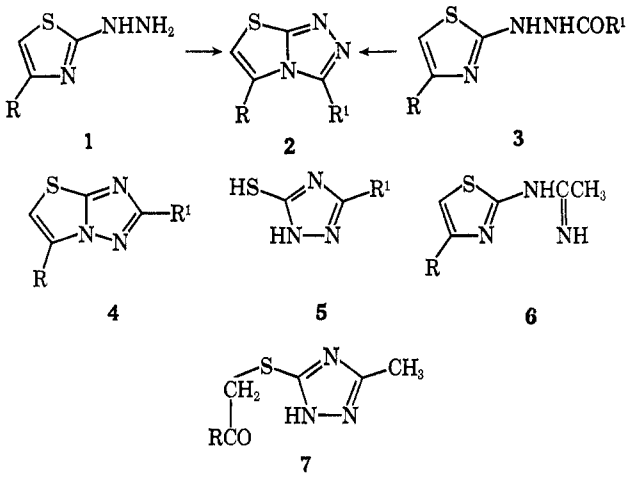
TABLE I

R	R¹	Mp, °C	Yield, %	Spectral characteristics,[c] Uv data,[d] λ_{max}, nm (log ϵ)	Ir data,[e] cm^{-1}	Nmr data[f] τ_3	τ_5	τ_6	Mass spectral data,[g] *m/e* (rel intensity)
Some Derivatives of Thiazolo[2,3-*c*]-*s*-triazole (2)[a,b]									
CH_3	H	111–112	60	248 (3.89), 204 (3.75)	3125, 3070, 1600, 1480	1.40 (s)	*7.48* (d, J = 1.20 Hz)	3.33 (q, J = 1.20 Hz)	140 (6), 139 (80), 112 (4), 71 (17), 67 (100)
CH_3	CH_3	181–182	20	246 (3.88), 201 (3.82)	3040, 2925, 1625, 1600	8.27 (s)	*7.50* (d, J = 1.20 Hz)	3.50 (q, J = 1.20 Hz)	154 (6), 153 (40), 112 (35), 71 (15), 67 (100)
CH_3	C_2H_5	96–97	16	247 (3.94), 207 (3.73)	3040, 2975, 1600, 1500	6.90 (q), *8.65* (t) (J = 7.50 Hz)	*7.50* (d, J = 1.20 Hz)	3.54 (q, J = 1.20 Hz)	168 (6), 167 (62), 112 (54), 71 (19), 67 (100)
CH_3	Ph	149	61	262 (4.07), 200 (4.23)	3050, 1595, 1450	2.42 (s)	*7.88* (d, J = 1.20 Hz)	3.39 (q, J = 1.20 Hz)	216 (11), 215 (75), 112 (80), 71 (20), 67 (100)
CH_3	SH	246–247	25	297 (4.25), 214 (3.90)	3100, 3000, 2720, 1600, 1530	*ca.* 6.7 (broad) (D_2O exchange)	*7.27* (d, J = 1.20 Hz)	3.35 (q, J = 1.20 Hz)	172 (7), 171 (78), 112 (30), 71 (4), 67 (100)
CH_3	SCH_3	108–110	92	267 (4.0), 202 (3.84)	3120, 1600, 1475	*7.23* (s)	*7.42* (d, J = 1.20 Hz)	3.48 (q, J = 1.20 Hz)	186 (9), 185 (100), 152 (40), 112 (44), 71 (24), 67 (100)
Ph	H	128	20	275 (4.06), 210 (4.03)	3080, 1615, 1600, 1470	1.20 (s)	2.44 (s)	3.00 (s)	202 (13), 201 (100), 174 (87), 129 (86), 103 (16), 77 (79), 51 (46)
Ph	CH_3	245	48	264 (3.92), 200 (4.34)	3025, 1610, 1580, 1500	*7.77* (s)	2.5 (s)	3.27 (s)	216 (12, 215 (78), 174 (100), 129 (77), 77 (72), 51 (35)
Ph	C_2H_5	145	43	263 (3.91), 202 (4.20)	3075, 2940, 1605, 1560	7.40 (q), 8.92 (t), (J = 7.50 Hz)	2.45 (s)	3.24 (s)	230 (13), 229 (79), 174 (100), 129 (50), 77 (40)
Ph	Ph	165	48	271 (4.17), 218 (4.27), 202 (4.50)	3050, 1550, 1490, 1450	2.83 (s)	2.83 (s)	3.12 (s)	278 (12), 277 (58), 174 (100), 129 (50), 77 (40)
Ph	SH	213–214	50	308 (3.92), 185 (4.15)	3075, 2900, 2700, 1590, 1560	*ca.* 6.4 (broad) (D_2O exchange)	2.46 (m)	2.77 (s)	234 (13), 233 (100), 174 (58), 129 (61), 103 (26), 77 (76), 51 (30)
Ph	SCH_3	166	46	275 (4.00), 197 (4.47)	3075, 2925, 1475, 1400	*8.25* (s)	2.48 (s)	3.25 (s)	248 (16), 247 (100), 214 (33), 174 (64), 147 (17), 129 (58), 103 (12), 77 (44), 51 (19)
Ph	NH_2	229–230	28	283 (3.76), 226 (4.01), 205 (4.20)	3350, 3280, 1625, 1550	4.78 (s) (D_2O exchange)	2.44 (s)	2.87 (s)	217 (12), 216 (100), 174 (63), 129 (63), 103 (15), 102 (30), 77 (80), 51 (50)
Some Derivatives of Thiazolo[3,2-*b*]-*s*-triazole (4)[h]									
CH_3	CH_3	68–69	63	246 (3.91), 201 (3.80)	3075, 3000, 1575, 1495	*7.43* (s)	*7.48* (d, J = 1.50 Hz)	3.45 (q, J = 1.50 Hz)	154 (10), 153 (100), 112 (36), 67 (80), 42 (36), 40 (66)
CH_3	Ph	124–125	84	258 (4.36), 223 (4.10), 203 (4.43)	3100, 1475, 1400	2.57–1.87 (m)	*7.47* (d, J = 1.50 Hz)	3.50 (q, J = 1.50 Hz)	216 (16), 215 (10), 103 (14), 77 (9), 72 (32), 71 (12)
Ph	Ph	137–138	72	262 (4.40), 198 (4.55)	3050, 1500 1470	3.08–2.32 (m)	3.08–2.32 (m)	3.48 (s)	278 (20), 277 (100), 174 (13), 134 (64), 129 (16), 103 (23), 77 (80), 76 (38), 51 (13)
Ph	CH_3	100–101	52	270 (4.14), 227 (4.18), 202 (4.24)	3050, 1550 1495	*7.40* (s)	2.52–2.94 (m)	3.01 (s)	216 (12), 215 (100), 174 (40), 129 (22), 103 (8), 77 (19), 51 (9)

[a] Satisfactory analyses (±0.35% for C, H, N) were reported for all compounds in table: Ed. [b] Registry numbers are, respectively, 26542-55-2, 26599-13-3, 26542-56-3, 26542-57-4, 26542-58-5, 26542-59-6, 26542-60-9, 26542-63-9, 26599-18-8, 26542-64-3, 26542-65-4, 26542-66-5, 26542-67-6. [c] Spectra were determined under the conditions given in footnotes *d–f*. Methyl resonances are in italics. [d] Methanol. [e] KBr. [f] $CDCl_3$. [g] At 70 eV. [h] Registry numbers are, respectively, 26542-68-7, 26542-69-8, 26542-70-1, 26542-71-2.



Reaction of the hydrazines **1** (R = CH_3, Ph) with carbon disulfide provided a convenient synthesis of the thiazolo[2,3-*c*]-*s*-triazole-3-thiols (**2**, R = CH_3, Ph; R^1 = SH). These were readily converted into the corresponding methylthio compounds with methyl iodide. Cyanogen bromide was found to react readily with 4-phenyl-2-thiazolylhydrazine (**1**, R = Ph), giving the 3-amino derivative of **2** (R^1 = NH_2). The structures of these products were evident from analytical and spectral data (Table I). They were found to be stable to acid, alkali, or heat, and no evidence for isomerization to the thiazolo[3,2-*b*]-*s*-triazole system was obtained.

Attempts to prepare authentic examples of **4** by lead tetraacetate cyclization of the amidines **6** failed. Also, amination of 2-aminothiazoles with hydroxylamine-*O*-sulfonic acid to the corresponding 1,2-diamino products was unsuccessful in this system, results similar to those obtained with 2-amino-1,3,4-thiadiazoles.[8] However, reaction of *s*-triazole-3-thiols **5** with α-halogeno ketones was found to be a very effective route to the thiazolo[3,2-*b*]-*s*-triazoles. The 5 substituent of the *s*-triazole nucleus had a pronounced effect on the ease of ring closure. Thus 5-phenyl-*s*-triazole-3-thiol (**5**, R^1 = Ph) with phenacyl bromide or chloroacetone gave the appropriately substituted thiazolo[3,2-*b*]-*s*-triazole system in greater than 70% yield using a 4-hr reaction period. Under the same conditions, 5-methyl-*s*-triazole-3-thiol gave the intermediate products **7** (R = CH_3, Ph); however, increasing the reaction period to 24 hr gave the thiazolo[3,2-*b*]-*s*-triazole system directly. Cyclization of **7** to a bicyclic system was effected with phosphoryl chloride in xylene but, instead of **4**, the thiazolo[2,3-*c*]-*s*-triazole system (**2**) was formed. This difference in behavior is understandable in terms of the influence of the reaction conditions on the basicity of the nitrogen atoms. Under thermal conditions, the more basic center is associated with N_1 (or N_2) but with phosphoryl chloride, N_4 would be more basic owing to the formation of an intermediate phosphorous compound[9] at N_1 (or N_2).

The nmr characteristics of these isomeric ring systems are particularly useful for structural determinations. The chemical shift of the 6 proton is in the range τ 2.77–3.54, the actual value depending upon the inductive character of the other substituents in the nucleus (Table I). The 6 proton is coupled in a characteristic way to the 5-methyl substituent (J = 1.20–1.50 Hz) and occurs as a sharp singlet in the 5-phenyl compounds. The observed chemical shift is consistent with that reported[10] for the 2 proton in 4-methylthiazole (τ 3.13), though in the latter the corresponding coupling constant (J = 1.00 Hz) is smaller. The magnitude of this benzylic coupling in the fused ring system agrees well with those found in other heteroaromatic systems[11] and, in this present case, may indicate some degree of bond fixation.

In 3,5-dimethylthiazolo[2,3-*c*]-*s*-triazole the chemical shift of the 3-methyl group is τ 8.27, whereas in 2,5-dimethylthiazolo[3,2-*b*]-*s*-triazole the chemical shift of the corresponding 2-methyl group has undergone a downfield shift of 0.84 ppm to τ 7.43. However, this juxtapositioning of the nitrogen atoms had very little effect on the chemical shifts of the 5 and 6 substituents (Table I).

The influence of phenyl groups on the chemical shifts of other ring substituents is interesting. Thus, in 5-phenylthiazolo[3,2-*c*]-*s*-triazole the chemical shift of the 3 proton is τ 1.20, a downfield shift of 0.20 ppm from that observed in the corresponding 5-methyl compound. Similarly, the chemical shift of the 3-methyl group has also undergone a small downfield shift (0.50 ppm) in the analogous 3-methyl compounds. This is most likely due to the inductive effect of the 5-phenyl group, as in 3-ethyl- and 3-methylthiothiazolo[3,2-*c*]-*s*-triazole the chemical shifts of the 3 substituents are now at a higher field than those observed in the corresponding 5-methyl compounds. This is not unexpected as steric requirements would tend to place these bulky 3 substituents in the shielding zone of the 5-phenyl group. This steric effect is also reflected in the ultraviolet absorption spectra of these compounds (Table I).

In the thiazolo[3,2-*b*]-*s*-triazole system, very little cross-ring interaction is evident. Thus, in 2,5-dimethylthiazolo[3,2-*b*]-*s*-triazole and 5-methyl-2-phenylthiazolo[3,2-*b*]-*s*-triazole, the chemical shifts of the 5-methyl groups are identical. Similarly, reversing the methyl–phenyl substitution pattern does not have an appreciable effect on the chemical shift of the 2-methyl group. These compounds also show clearly the influence of a nuclear nitrogen atom on the ortho proton in a phenyl substituent (Table I).

In the mass spectra of these fused ring systems (Table I), molecular ions were obtained for all compounds studied. As has been found in other fused *s*-triazole systems, fragmentation of the *s*-triazole moiety was observed as the initial decomposition. Thus, in 3,5-dimethylthiazolo[2,3-*c*]-*s*-triazole, acetonitrile was lost from the molecular ion, giving an ion, m/e 112. This then lost HCS to give an ion, m/e 67 (100%), which is common to all the 5-methyl compounds. The corresponding ion in the 5-phenyl compounds was observed at m/e 129 and was a relatively intense ion. The mass spectra of 3-methyl-5-phenylthiazolo[2,3-*c*]-*s*-triazole and 2-methyl-5-phenylthiazolo[3,2-*b*]-*s*-triazole are practically identical. They illustrate the danger in

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making structural assignments in isomeric systems based on mass spectral data.

Experimental Section[12]

General Procedures for the Cyclization of 2-Thiazolylhydrazines. A. With Carboxylic Acids.—4-Methyl-2-thiazolylhydrazine[13] (0.5 g) and formic acid (1.0 ml) were refluxed for 6 hr, the excess of formic acid removed under reduced pressure, and the residue recrystallized from benzene (charcoal) affording colorless needles of **2** (R = CH_3; R^1 = H), 0.6 g, mp 111–112° (Table I). A minimum reflux period of 6 hr was essential to prevent contamination of the cyclized product with the hydrazide **3**.

B. With Ortho Esters.—4-Methyl-2-thiazolylhydrazine (1.0 g) and ethyl orthoacetate (5 ml) were heated under reflux for 6 hr. Reaction work-up as above and final recrystallization from methanol–benzene afforded **2** (R = R^1 = CH_3) as colorless needles, mp 181–182°.

C. With Carbon Disulfide.—4-Phenylthiazol-2-ylhydrazine[5b] (1.0 g), methanol (50 ml), potassium hydroxide (0.3 g), and carbon disulfide (3 ml) were refluxed for 4 hr. After removal of the methanol, dilute potassium hydroxide was added and the alkaline solution was filtered. After precipitation with dilute hydrochloric acid, **2** (R = Ph; R^1 = SH) crystallized from methanol–benzene (charcoal) as colorless needles, mp 213–214°.

D. With Cyanogen Bromide.—4-Phenylthiazol-2-ylhydrazine (1.0 g) in methanol (50 ml of 75%) and cyanogen bromide (0.5 g) were heated under reflux for 4 hr. The cooled reaction mixture was poured into ether (1000 ml) and the red solid that separated was dissolved in water and sodium acetate was added. Crystallization of the free base from methanol–benzene (charcoal) afforded colorless needles of **2** (R = Ph; R^1 = NH_2), mp 229–230°.

E. Phosphoryl Chloride Cyclization of the Acylhydrazines.—2-(4-Phenylthiazol-2-yl)acethydrazide (1.0 g), dry xylene (20 ml), and phosphoryl chloride (2 g) were refluxed for 8 hr. The cooled reaction mixture was diluted with petroleum ether (bp 60–80°) and the supernatant liquor decanted. The residue was dissolved in water, ammonium hydroxide added, and the product extracted with chloroform. The chloroform extract was dried (anhydrous Na_2SO_4) and the solvent removed; the residue crystallized from methanol–benzene (charcoal) forming colorless needles of **2** (R = Ph; R^1 = CH_3), mp 245°.

Reaction of 5-Methyl(phenyl)thiazolo[2,3-*c*]-*s*-triazole-3-thiols with Methyl Iodide.—The thiol (0.7 g), dissolved in water and *ca.* 0.5 ml of potassium hydroxide (50%), was shaken with methyl iodide (5 ml) for 5 min. Excess of methyl iodide was evaporated and the residue recrystallized from benzene (charcoal), forming colorless needles of the products described in Table I.

Reaction of 5-Phenyl-*s*-triazole-3-thiol (5, R^1 = Ph) with Phenacyl Bromide (or Chloroacetone).—The thiol (0.01 mol) in absolute ethanol (100 ml) was treated with phenacyl bromide (0.01 mol) and the reaction mixture refluxed for 4 hr. Ethanol was evaporated and the residue was treated with a concentrated, aqueous solution of sodium acetate. The product which separated was recrystallized from benzene–petroleum ether (bp 60–80°) forming colorless needles of **4** (R = R^1 = Ph), mp 137–138° (Table I).

Reaction of 5-Methyl-*s*-triazole-3-thiol (5, R^1 = CH_3) with Chloroacetone.—The thiol (0.01 mol), chloroacetone (0.01 mol), and absolute ethanol (100 ml) were refluxed for 4 hr. The residue, after evaporation of the ethanol, was dissolved in water and aqueous sodium acetate added. Water was evaporated and the residue extracted several times with hot chloroform (20 ml). Evaporation of the chloroform and recrystallization of the residue from benzene gave small, colorless irregular prisms of 3-(acetonylthio)-5-methyl-*s*-triazole: mp 125–126° (47%); ir (KBr) 3150, 3050 (CH), 1720 (CO), 1580 cm^{-1} (C=N); $\lambda_{max}^{CH_3OH}$ 207 nm (log ϵ 3.62); mass spectrum (70 eV) *m/e* (rel intensity) 171 (26), 129 (100), 128 (52), 96 (12), 84 (24).

Anal. Calcd for $C_6H_9N_3OS$: C, 42.10; H, 5.30; N, 24.55. Found: C, 41.89; H, 5.26; N, 24.39.

Similarly, **3-(phenacylthio)-5-methyl-*s*-triazole** crystallized from benzene as colorless needles: mp 120–121° (70%); ir (KBr) 2900, 2850 (CH), 1680 (CO), 1595 cm^{-1} (C=N); $\lambda_{max}^{CH_3OH}$, nm (log ϵ), 280 (3.16), 247 (4.08), 202 (4.33); mass spectrum (70 eV) *m/e* (rel intensity) 233 (7), 205 (5), 191 (5), 106 (100), 91 (4), 78 (15), 77 (40), 51 (13).

Anal. Calcd for $C_{11}H_{11}N_3OS$: C, 56.65; H, 4.72; N, 18.02. Found: C, 56.50; H, 4.72; N, 17.90.

Reflux of the above 3-thio compounds with phosphoryl chloride in xylene for 8 hr gave the corresponding thiazolo[2,3-*c*]-*s*-triazoles. However, extension of the reaction time to 24 hr in the initial condensation with the α-halo ketone resulted in formation of the thiazolo[3,2-*b*]-*s*-triazoles.

***N*-(4-Phenylthiazol-2-yl)acetamidine.**—2-Amino-4-phenylthiazole (8.8 g, 0.05 mol) and acetonitrile (3.0 g, 0.07 mol) were mixed and anhydrous aluminum chloride (6.6 g, 0.05 mol) was added. After the vigorous reaction had subsided, the reaction mixture was heated at 170–175° for 3 hr and then, on cooling, decomposed by the cautious addition of water. After basification of the resultant solution with sodium hydroxide, it was extracted with ether, the ether extract treated with charcoal, and the ether then evaporated. After recrystallization of the residue from ether–petroleum ether (bp 60–80°), the amidine was obtained as colorless needles: mp 108–110°; 5.6 g (52%); ir (KBr) 3280 (NH), 3020 (CH), 1630 cm^{-1} (C=N); $\lambda_{max}^{CH_3OH}$, nm (log ϵ), 295 sh (4.16), 283 (4.22), 277 sh (4.18), 242 (4.10), 212 (4.15).

Anal. Calcd for $C_{11}H_{11}N_3S$: C, 60.82; H, 5.07; N, 19.35. Found: C, 60.92; H, 5.07; N, 19.25.

Registry No.—3-(Acetonylthio)-5-methyl-*s*-triazole, 26542-72-3; 3-(phenacylthio)-5-methyl-*s*-triazole, 26542-73-4; *N*-(4-phenylthiazol-2-yl)acetamidine, 26542-74-5.

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(12) All evaporations were done under reduced pressure using a rotatory evaporator. Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer and infrared spectra were measured on a Perkin-Elmer Model 337 infrared spectrophotometer. Nmr spectra were determined on a Varian A-60 spectrometer using TMS as internal standard and mass spectra were measured on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Melting points were taken in capillaries and microanalyses were by Galbraith Laboratories, Inc., Knoxville, Tenn., and Instranal Laboratories, Rensselaer, N. Y.

(13) H. Beyer and G. Wolter, *Chem. Ber.*, **85**, 1077 (1952).