K_2CO_3 (aqueous). The amidine was then distilled, collecting the fraction between 179 and 181° (lit.[14] bp 181°).

To 1 g (0.0078 mol) of *N,N*-diethylaminopropionamidine was added 2.74 g (0.0156 mol) of benzenesulfonyl chloride and 10 ml of sodium hydroxide. The reaction mixture was heated on a steam bath for 5 min and extracted with chloroform. The chloroform layer was dried (Na_2SO_4) and evaporated to dryness under reduced pressure. The resulting white solid was recrystallized from ether three times to give the analytical sample of *N,N*-diethylamino-*N*-benzenesulfonylpropionamidine (**12**): mp 95.5–96.5°; nmr ($CHCl_3$-*d*) δ 1.18 (m, 9, CH_3), 3.18 (m, 6, CH_2), 7.66 (m, 5, ArH).

Anal. Calcd for $C_{13}H_{20}N_2O_2S$: C, 58.23; H, 7.53; N, 10.45. Found: C, 58.00; H, 7.51; N, 10.37.

Registry No.—**7a**, 25866-46-0; **7b**, 25866-47-1; **7c**, 25866-48-2; **7d**, 25907-88-4; **8e**, 25866-49-3; **8f**, 25907-89-5; **9a**, 25907-90-8; **9b**, 25907-91-9; **9c**, 25866-50-6; **9d**, 25957-51-1; **9e**, 25866-51-7; **11**, 25866-52-8; **12**, 25866-53-9.

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1,2,4-Triazoles. XXIV. Isomerization of *s*-Triazolo[4,3-*c*]quinazoline Derivatives[1]

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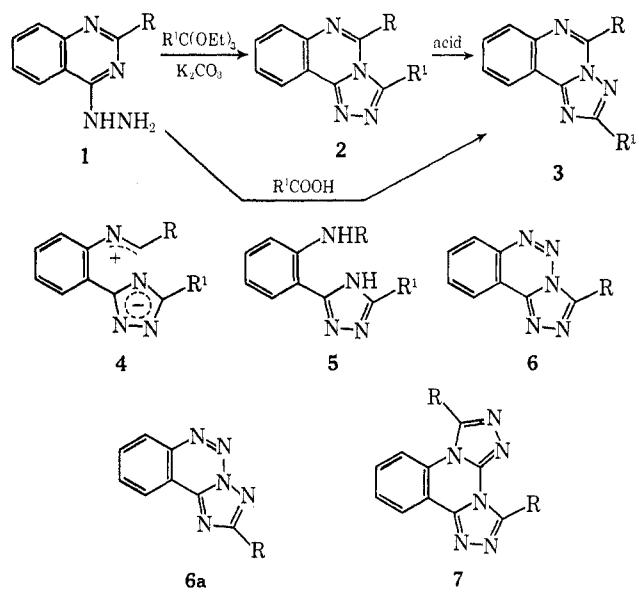
s-Triazolo[4,3-*c*]quinazolines, under the influence of acid or heat, underwent an extremely facile isomerization to *s*-triazolo[1,5-*c*]quinazolines. With alkali, ring opening occurred to 3-(2-aminophenyl)-*s*-triazoles which, with nitrous acid, gave the *s*-triazolo[4,3-*c*][1,2,3]benzotriazine system. Reduction of *s*-triazolo[1,5-*c*]quinazolines with sodium borohydride occurred at the 5,6 bond. Cyclization of 2,4-dihydrazinoquinazoline with ortho esters yielded bis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazolines.

Isomerization in ring-fused *s*-triazoles induced by acid, base, or heat has been reported for several of these ring systems.[2] A particularly facile isomerization was observed with derivatives of the *s*-triazolo[4,3-*a*]-pyrimidine[3a] and *s*-triazolo[4,3-*c*]pyrimidine[3b] systems, and we now report an even more facile isomerization of the *s*-triazolo[4,3-*c*]quinazoline system to the *s*-triazolo[1,5-*c*]quinazoline system.

The synthesis of a fused *s*-triazole in which the 3,4 side of the *s*-triazole moiety is involved in the fusion is possible from a suitable 2-heterylhydrazine and carboxylic acids or ortho esters.[4] Thus, reaction of 4-quinazolylhydrazine (**1**, R = H) with aliphatic acids or ortho esters should give 3-substituted *s*-triazolo[4,3-*c*]quinazolines (**2**). We have now found that reaction of the hydrazine (**1**) with aliphatic acids always yielded the *s*-triazolo[1,5-*c*]quinazolines (**3**) by an extremely facile *in situ* rearrangement of the [4,3-*c*] system (**2**). This rearrangement could also be effected by gentle warming of the isomer **2** with carboxylic acids or by heating above the melting point.

It was possible to obtain the *s*-triazolo[4,3-*c*]quinazoline system (**2**) from the hydrazine and ortho esters as long as the reaction was carried out in the presence of potassium carbonate (Table I). Omission of the potassium carbonate always resulted in a mixture of the two isomers being formed, no doubt owing to traces of the appropriate acid (detected by glc) in the redistilled ortho esters. With triethyl orthopropionate, however, isomerization of the expected [4,3-*c*] system did not occur over a 16-hr reaction period, but the isomerization was essentially complete over a 48-hr period in the absence of potassium carbonate.



Substituents in the 2 position of the quinazoline nucleus exerted a predictable effect on the isomerization. 2-Methylquinazolin-4-ylhydrazine (**1**, R = CH_3) and ortho esters–potassium carbonate should yield 5-methyl-*s*-triazolo[4,3-*c*]quinazolines (**2**, R = CH_3), but in all cases isomerization occurred with such ease that only mixtures of the two isomers could be isolated. On the other hand, 2-phenylquinazolin-4-ylhydrazine (**1**, R = Ph) underwent ring closure with ortho esters–potassium carbonate to 5-phenyl-*s*-triazolo[4,3-*c*]quinazolines (**2**,

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TABLE I

R¹	R	Mp, °C	Yield, %	Nmr data,[b] chemical shift, τ (ppm) R¹	R	Uv data, $\lambda_{max}^{CH_3OH}$, nm (log ε)	Mass spectral data,[c] M⁺
			Some *s*-Triazolo[4,3-*c*]quinazolines (**2**)[a]				
H	H	213–214	80	0.5	0.6	240 (4.60)	170
CH_3	H	231–232	80	7.2	0.6	250 (4.66)	184
Et	H	187–188	90	6.8	0.6	240 (4.58)	198
H	Ph	205–206[d]	80	0.6	1.3–2.5	245 (4.7) 290 (4.2)	246
Et	Ph	168–169	70	6.7	1.3–2.5	245 (4.6) 290 (4.1)	274
			Some *s*-Triazolo[1,5-*c*]quinazolines (**3**)				
H	H	109–110	75	1.4	0.6	240 (4.39)	170
CH_3	H	129–130	80	7.4	0.6	240 (4.79)	184
Et	H	86–87	65	7.2	0.6	240 (4.62)	198
H	Ph	184–185	87	1.4	1.3–2.5	245 (3.96)	246

[a] Satisfactory analytical values (±0.35 for C, H, and N) were reported for all compounds in this table: Ed. [b] Determined in $CDCl_3$. [c] Determined at 70 eV. [d] Lit.[5] mp 204–206°.

R = Ph; R¹ = H) without isomerization, thus substantiating an earlier claim[5] to the synthesis of **2** (R = Ph; R¹ = H). Isomerization of **2** (R = Ph) and its 3-alkyl derivatives to the corresponding isomeric system **3** was readily effected by extended reflux in acid solution.

These data indicate that in a reported synthesis[6] of 3-phenyl-*s*-triazolo[4,3-*c*]quinazoline (**2**, R = H; R¹ = Ph) by the cyclization of 4-benzhydrazidoquinazoline isomerization to the corresponding [1,5-*c*] system might have occurred. As the product isolated was stable to long reflux in acid solution, it appears that isomerization had actually occurred in the initial preparation and that the product should be regarded as 2-phenyl-*s*-triazolo-[1,5-*c*]quinazoline (**3**, R = H; R¹ = Ph).

The facility with which the above isomerizations occurred made it important to synthesize a representative *s*-triazolo[1,5-*c*]quinazoline derivative by an unambiguous route. Usual procedures for obtaining [1,5] fused *s*-triazole systems, such as dehydrogenation of suitable amidines or ring closure of 1,2-diaminopyridinium salts with acyl chlorides,[7] were precluded by the unavailability of the required precursors. However, a recent synthesis[8] of 2-amino-5-methyl-*s*-triazolo[1,5-*c*]quinazoline (**3**, R = CH_3; R¹ = NH_2), from aminoguanidine and 4-oxo-4H-3,1-benzoxazine provided a suitable route to the desired product. Deamination[9] of **3** (R = CH_3; R¹ = NH_2) with hypophosphorous acid gave a product identical with that obtained by ortho ester or acid ring-closure of 2-methylquinazolin-4-ylhydrazine (Table I). The spectral characteristics of the isomeric system (Table I) clearly differentiate between the respective structures. In particular, the high field chemical shifts of the 2 substituents in 2-substituted *s*-triazolo[1,5-*c*]quinazolines when compared with the chemical shifts of the corresponding 3 substituents in 3-substituted *s*-triazolo-[4,3-*c*]quinazolines readily enable assignments to the particular isomeric system to be made.

The above isomerization can be regarded as involving a covalent-type hydration of the 5,6 double bond of **2** followed by ring opening and subsequent ring closure at N-1 of the *s*-triazole nucleus. As the isomerization can also be effected by dry heat (more slowly), an alternative mechanistic hypothesis involving a zwitterionic intermediate such as **4**, may also be postulated.

This isomerization is essentially a variation of the Dimroth rearrangement and recent studies have shown[10] that in the quinazolines such isomerizations occur with extreme ease in the presence of alkali. Thus, the action of base on *s*-triazolo[4,3-*c*]quinazolines and also on *s*-triazolo[1,5-*c*]quinazolines was of particular interest.

Treatment of *s*-triazolo[4,3-*c*]quinazoline (**2**, R = R¹ = H) with hot aqueous sodium hydroxide gave 3-(2-aminophenyl)-*s*-triazole (**5**, R = R¹ = H) whose structure was confirmed by deamination to 3-phenyl-*s*-triazole. That the reaction involved an initial attack of hydroxide ion at the 6 position, rather than abstraction of the 6 proton which was observed in the conversion of *s*-triazolo[3,4-*a*]phthalazine into 3-(2-cyanophenyl)-*s*-triazole,[11] was established by the isolation of 3-(2-benzamidophenyl)-*s*-triazole (**5**, R = CO Ph; R¹ = H) by the action of hot base on 5-phenyl-*s*-triazolo-[4,3-*c*]quinazoline (**2**, R = Ph; R¹ = H). It appears that under these rearrangement conditions hydrolysis of the intermediate amide is faster than ring closure to the isomeric [1,5-*c*] system. The latter system also underwent analogous ring-opening reactions with a variety of substituents in the nucleus.

3-(2-Aminophenyl)-*s*-triazole (**5**, R = R¹ = H), on reaction with nitrous acid, gave *s*-triazolo[4,3-*c*]-[1,2,3]benzotriazine (**6**), a new heterocyclic ring system. The same product was also obtained from 4-(1,2,3)-benzotriazinylhydrazine and ethyl orthoformate. The available data does not exclude representation of this product as *s*-triazolo[1,5-*c*][1,2,3]benzotriazine (**6a**) which would be formed by ring closure of the intermediate diazo compound at N-1 of the *s*-triazole nucleus. If the latter structure were correct, it could only be formed from 1,2,3-benzotriazin-4-ylhydrazine by ring opening and rearrangement of the initial *s*-triazolo-[4,3-*c*][1,2,3]benzotriazine isomer (**6**). Though no isomerizations of ring-fused *s*-triazole systems reported to date have involved fission and re-formation of N–N

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bonds, it should be noted that solutions of condensed *v*-triazines have been found to be in equilibrium with the corresponding diazo isomer.[12] In **6** a similar situation can be readily envisaged, and the assignment of this structure can only be regarded as tentative at this stage. This internal diazonium cyclization reaction is a convenient route to heterocycles of this type and several examples of analogous ring systems have been described in the literature.[13]

The 5,6 double bond of 2-methyl-*s*-triazolo[1,5-*c*]quinazoline was found to be the site of reduction with sodium borohydride. The product, 5,6-dihydro-2-methyl-*s*-triazolo[1,5-*c*]quinazoline was readily identified from its nmr spectrum which showed methylene protons at τ 4.51 and an exchangeable NH proton at τ 4.25.

2,4-Dihydrazinoquinazoline (**1**, R = $NHNH_2$) is a suitable precursor for the synthesis of the bis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazoline system (**7**). Ring closure readily occurred with ortho esters and this is the first example of a tetracyclic system derived from quinazoline. Though possibilities exist for isomerization during the reaction, only one product was obtained. Ready hydrolysis of **7** occurred with hot, dilute acid yielding 2,4-dihydrazinoquinazoline, thus confirming the assigned structure. Unlike the tricyclic systems **2** and **3**, the tetracyclic nucleus was stable to hot alkali.

Experimental Section[14]

The hydrazinoquinazolines were prepared by established procedures.[15] Minor variations in reaction work-up, especially the use of two-phase systems (water-chloroform at 0° for 3 hr) for the decomposition of the intermediate chloroquinazoline-phosphoryl chloride complexes, resulted in significant increases in overall yields.

Cyclization of 4-Quinazolinylhydrazines. A. With Ortho Esters–Potassium Carbonate.—The hydrazine (1.0 g), triethyl orthoformate (50 ml) and anhydrous potassium carbonate (0.5 g) were heated under reflux for 30 min. The product precipitated on cooling and, after recrystallization from ethanol, *s*-triazolo[4,3-*c*]quinazoline separated as fine, colorless needles: 0.6 g (64%); mp 213–214°; ir (KBr) 3050 (C–H), 1610 (C=N), 1525 (C=C) cm^{-1}.

The products prepared by this general procedure are described in Table I and their ir characteristics were consistent with those described above.

B. With Aliphatic Acids.—The hydrazine (1.0 g) was heated under reflux with formic acid (50 ml) for 30 min. After evaporation of excess acid, the residue crystallized from ethanol and *s*-triazolo[1,5-*c*]quinazoline was obtained as fine, colorless needles: 0.5 g (53%); mp 113–114°; ir (KBr) 3050 (C–H), 1610 (C=N), 1510 (C=C) cm^{-1}. Table I shows products prepared by this general procedure.

Isomerization of the *s*-Triazolo[4,3-*c*]quinazoline to the *s*-Triazolo[1,5-*c*]quinazoline System. A. By Acid.—The *s*-triazolo[4,3-*c*]quinazoline was refluxed in the corresponding aliphatic acid for 30 min. The acid was removed under reduced pressure and the product recrystallized from ethanol. The products were identical with those prepared by method B above.

B. By Heat.—The *s*-triazolo[4,3-*c*]quinazolines were heated above their melting points and, after cooling to room temperature, purified as above.

Ring Opening of *s*-Triazolo[4,3-*c*]quinazolines with Alkali.—*s*-Triazolo[4,3-*c*]quinazoline (or the [1,5-*c*] isomer) (1.0 g) and aqueous KOH (10%, 50 ml) were heated under reflux for 1 hr. After neutralization, the reaction mixture was extracted with ether, the ether extract dried (Na_2SO_4) and the residue left after evaporation of the ether recrystallized from benzene to give 3-(2-aminophenyl)-*s*-triazole as colorless needles: 0.45 g (50%); mp 144–145°; ir (KBr) 3400 (NH_2), 3100 (NH), 1610 (C=N), 1560 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 220 nm (log ϵ 3.51), 253 (3.10), 320 (2.75); nmr (CH_3CN) τ 4.0 (b, 2, NH_2), 3.40–2.20 (m, 4, aromatic), 1.78 (s, 1, H_5); mass spectrum, M^+, *m/e* (rel intensity) 164 (100).

Anal. Calcd for $C_8H_8N_4$: C, 59.97; H, 5.04; N, 34.97. Found: C, 60.28; H, 5.01; N, 34.73.

In a similar fashion, treatment of the appropriate *s*-triazolo-[4,3-*c*]- or -[1,5-*c*]quinazolines gave the following products.

3-(2-Aminophenyl)-5-methyl-*s*-triazole: colorless needles (85%); mp 153–154°; ir (KBr) 3400 (NH_2), 3150 (NH), 3050 (C–H), 1610 (C=N), 1570 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 219 nm (log ϵ 4.63), 250 (4.11), 318 (3.78); nmr (CH_3CN) τ 7.60 (s, 3, 5-CH_3), 4.05 (b, 2, NH_2), 3.5–2.3 (m, 4, aromatic); mass spectrum M^+, *m/e* (rel intensity) 124 (100).

Anal. Calcd for $C_9H_{10}N_4$: C, 61.96; H, 5.70; N, 32.05. Found: C, 62.03; H, 5.79; N, 32.06.

3-(2-Aminophenyl)-5-phenyl-*s*-triazole: colorless needles (90%); mp 189–190°; ir (KBr) 3370 (NH_2), 3100 (NH), 1610 (C=N), 1560 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 210 nm (log ϵ 4.73), 230 (4.80), 260 (4.50), 320 (3.94); nmr (CH_3CN) τ 2.3–2.0 (m, aromatic); mass spectrum, M^+, *m/e* (rel intensity) 235 (100).

Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.29; H, 5.26; N, 23.75.

Treatment of 3-(2-Aminophenyl)-5-methyl-*s*-triazole with Nitrous Acid.—A mixture of sulfuric acid (20 ml, 8 *N*) and water (10 ml) at −10° was treated with sodium nitrite (0.57 g) added over 15 min followed by hypophosphorous acid (3 ml). Maintaining the temperature below −10°, 3-(2-aminophenyl)-5-methyl-*s*-triazole (2.0 g, 0.1 mol) was added in small portions with continuous stirring. After 2 hr at −10°, the reaction mixture was warmed at 60° for 2 hr and then neutralized with KOH solution. The 3-methyl-*s*-triazolo[4,3-*c*][1,2,3]benzotriazine that separated was recrystallized from benzene–petroleum ether (bp 60–80°) forming colorless needles: 1.4 g (75%); mp 163–164°; ir (KBr) 3075 (C–H), 1610 (C=N), 1580 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 248 nm (log ϵ 4.52), 290 (3.20); nmr ($CDCl_3$) τ 7.40 (s, 3, 3-CH_3), 2.2–1.3 (m, 4, aromatic); mass spectrum M^+, *m/e* (rel intensity) 185 (44).

Anal. Calcd for $C_9H_7N_5$: C, 58.37; H, 3.81; N, 37.82. Found: C, 58.17; H, 3.71; N, 38.11.

3-Phenyl-5-methyl-*s*-triazole was extracted with chloroform from the slightly basic reaction mixture and crystallized from benzene as colorless needles: mp 163–164° (lit.[16] mp 166°).

Similarly, ***s*-triazolo[4,3-*c*][1,2,3]benzotriazine** crystallized from benzene as colorless needles: yield 90%; mp 135–136°; ir (KBr) 3100 (C–H), 1620 (C=N), 1590 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 238 nm (log ϵ 4.81), 280 (4.00); nmr ($CDCl_3$) τ 2.2–1.3 (m, aromatic); mass spectrum M^+, *m/e* (rel intensity) 170 (45).

Anal. Calcd for $C_8H_5N_5$: C, 56.15; H, 2.92; N, 40.94. Found: C, 55.95; H, 2.79; N, 41.17.

Cyclization of 1,2,3-Benzotriazin-4-ylhydrazine with Ortho Esters.—The above hydrazine[17] (1.0 g) was refluxed in triethyl orthoformate (25 ml) with K_2CO_3 for 1 hr. The product precipitated upon cooling and was recrystallized from ethanol. The product was identical in every respect with that prepared above.

General Procedure for the Preparation of Bis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazolines.—2,4-Dihydrazinoquinazoline (2.0 g, 0.01 mol) and triethyl orthoformate (40 ml) were heated under reflux for 1 hr. The excess triethyl orthoformate was removed under reduced pressure and the residue was purified by sublimation *in vacuo* [180° (0.1 mm)]: 1.2 g (60%); mp 341–342°; ir (KBr) 3050 (C–H), 1600 (C=N), 1480 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 240 nm; mass spectrum M^+, *m/e* (rel intensity) 210 (100).

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(14) Spectral characterization of products was carried out on the following instrumentation: ir, Perkin-Elmer Model 337 spectrophotometer; uv, Cary Model 14 spectrophotometer; nmr, Varian A-60 spectrometer using TMS as internal standard; mass spectra, Hitachi Perkin-Elmer RMU 6E mass spectrometer, using the direct inlet probe at ~150° and 70 eV. All evaporations were done under reduced pressure using a rotavap apparatus and mps were taken in capillaries. Microanalyses were by Galbraith Laboratories, Inc., Knoxville, Tenn., and Instranal Laboratories, Rensselaer, N. Y.

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Anal. Calcd for $C_{10}H_6N_6$: C, 57.13; H, 2.87; N, 39.98. Found: C, 56.93; H, 2.84; N, 39.85.

Similarly, **3,7-dimethylbis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazoline** was purified by sublimation *in vacuo* [160° (0.1 mm)]: 1.9 g (80%); mp 315–316°; ir (KBr) 3125 (C–H), 1610 (C=N), 1525 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 240 nm; nmr ($CDCl_3$) τ 7.39 (s, 3, CH_3), 7.31 (s, 3, CH_3), 2.6–1.5 (m, 4, aromatic); mass spectrum M^+, *m/e* (rel intensity) 238 (100).

Anal. Calcd for $C_{12}H_{10}N_6$: C, 60.49; H, 4.23; N, 35.27. found: C, 60.25; H, 4.25; N, 35.24.

3,7-Diethylbis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazoline was also purified by sublimation *in vacuo* [150° (0.1 mm)]: 1.7 g (65%); mp 258–259°; ir (KBr) 2980 (C–H), 1600 (C=N), 1580 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 240 nm; mass spectrum M^+, *m/e* (rel intensity) 266 (100).

Anal. Calcd for $C_{14}H_{14}N_6$: C, 63.14; H, 5.29; N, 31.56. Found: C, 63.22; H, 5.22; N, 31.74.

Reaction of Bis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazoline with Dilute Acid.—Bis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazoline (2.0 g, 0.008 mol) and 10% HCl (40 ml) were heated under reflux for 0.5 hr. The solvent was removed under reduced pressure. The residue crystallized from ethanol as fine, yellow needles. The product was identical in every respect with an authentic sample of 2,4-dihydrazinoquinazoline: 1.5 g (90%); mp 226–227° dec (lit.[15] mp 226–227° dec); ir 3450 (NH_2), 3050 (NH), 1650 (C=N), 1620 (NH), 1560 (C=C) cm^{-1}.

Sodium Borohydride Reduction of 2-Methyl-*s*-triazolo[1,5-*c*]quinazoline.—The quinazoline (1.0 g, 0.006 mol), methanol (50 ml), and excess sodium borohydride (1.6 g) were stirred at room temperature for 17 hr. The reaction mixture was evaporated to dryness under reduced pressure, and the crude residue was dissolved in water and the insoluble material filtered. The solution was then extracted with chloroform, dried (Na_2SO_4), and removed under reduced pressure. The crude product crystallized from benzene as fine, colorless needles: 0.6 g (60%); mp 150–151°; ir (KBr) 3200 (NH), 1640 (C=N), 1600 (NH), 1550 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 230 nm (log ϵ 3.19); nmr ($CDCl_3$) τ 7.58 (s, 3, 2-CH_3), 4.51 (s, 2, $-CH_2-$), 3.3–2.1 (m, 4, aromatic), 4.25 (b, 1, –NH); mass spectrum M^+, *m/e* (rel intensity) 186 (100).

Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.28; H, 5.50; N, 29.87.

Registry No.—**2** (R[1] = H; R = H), 234-74-2; **2** (R[1] = Me; R = H), 25518-06-3; **2** (R[1] = Et; R = H), 25518-07-4; **2** (R[1] = H; R = Ph), 6506-59-8; **2** (R[1] = Et; R = Ph), 25518-09-6; **3** (R[1] = H; R = H), 234-74-2; **3** (R[1] = Me; R = H), 25518-11-0; **3** (R[1] = Et; R = H), 25518-12-1; **3** (R[1] = H; R = Ph), 25518-13-2; **5** (R[1] = R = H), 25518-14-3; **5** (R[1] = Me; R = H), 25568-69-8; **5** (R[1] = Ph; R = H), 25518-15-4; **6**, 25518-16-5; **6** (R = Me), 25518-17-6; **7**, 25518-18-7; **7** (R′ = R = Me), 25518-19-8; **7** (R[1] = R = Et), 25518-20-1; 5,6-dihydro-2-methyl-*s*-triazolo[1,5-*c*]quinazoline, 27111-63-3.

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Mesoionic Compounds. XI. Mesoionic Compounds of the 1,2,3-Triazole Series[1]

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Cyclization of ethyl N-methyl-N-arylazoaminoacetates with thionyl chloride gave anhydro-3-aryl-4-hydroxy-1-methyl-1,2,3-triazolium hydroxides. The corresponding N-methyl-N-arylazoaminoacetonitriles also underwent ready cyclization to anhydro-4-acetylimino-3-aryl-1-methyl-1,2,3-triazolium hydroxides with acetyl chloride, followed by treatment with base. Several cycloaddition reactions as well as chemical and spectral characteristics of this mesoionic system are described. In contrast to other mesoionic systems, protonation occurred readily at the exocyclic oxygen atom which was also the site of alkylation with triethyloxonium fluoroborate.

Since introduction of the original concept of mesoionic compounds,[2] comparatively few new systems have been described. As part of a general study of this interesting class of compounds, we have been investigating the synthesis of new types[3a] and now report our studies which have led to new mesoionic compounds of the 1,2,3-triazole series.[3b]

Cyclodehydration procedures have usually been used in the synthesis of mesoionic systems[4] and a variation of this approach was found to be effective in the 1,2,3-triazole system. Condensation of benzenediazonium chloride (**1**, R = Ph) with ethyl sarcosinate under carefully controlled conditions gave ethyl N-methyl-N-phenylazoaminoacetate (**2**, R = Ph) in 53% yield. Attempts to condense benzene–diazonium chloride with sarcosine itself under analogous conditions were unsuccessful, thus precluding the usual cyclodehydration of an appropriately substituted acid to the mesoionic system. Cyclization of the ester (**2**, R = Ph) with thionyl chloride–pyridine readily gave anhydro-4-hydroxy-3-phenyl-1-methyl-1,2,3-triazolium hydroxide (**4**, R = Ph) together with a small amount of a sulfur-containing product which has been identified as the sulfide (**6**). This sulfide was also obtained by the action of thionyl chloride–pyridine on the amide (**3**) as well as from the mesoionic system (**4**) and sulfur monochloride. Its structure was evident from analytical data which established the molecular formula as $C_{18}H_{16}N_6SO_2$ and from spectral data where the nmr spectrum was similar in all respects to that of **4** except that the 5-proton was absent. Use of *p*-toluenediazonium chloride in this reaction gave analogous products.

Analytical and spectral data clearly showed that ring closure to these mesoionic compounds had occurred. Particularly important in this respect were the ν_{CO} at 1650 cm^{-1} in the infrared spectra and a sharp singlet at

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