1,2,4-Triazoles. XVIII. The Synthesis of 5H-*s*-Triazolo[5,1-*c*]-*s*-triazole and Its Derivatives[1]

K. T. POTTS[1] AND C. HIRSCH

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208

Received May 4, 1967

Dehydrogenative ring closure of 3-benzylidenehydrazino-*s*-triazoles gave exclusively 3-phenyl-5H-*s*-triazolo-[5,1-*c*]-*s*-triazoles. Cyclization of triaminoguanidine with cyanogen bromide yielded 3,6,7-triamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole, whereas, with carbon disulfide and alkali, 4-amino-3-hydrazino-*s*-triazole-5-thiol and 1,3,4-thiadiazole-2,5-dithiol were formed. These reagents with 3-hydrazino-*s*-triazoles and 4-amino-3-hydrazino-*s*-triazoles also gave appropriately substituted derivatives of the 5(7)H-*s*-triazolo[5,1-*c*]-*s*-triazole system. Deamination and desulfurization procedures were used to interrelate the products formed in these cyclization reactions and enabled the parent ring system to be obtained for the first time.

The fusion of two *s*-triazole nuclei results in four isomeric ring systems: the 5(7)H-*s*-triazolo[5,1-*c*]-*s*-triazole system (**1**); the 7H-*s*-triazolo[3,4-*c*]-*s*-trizole system (**2**); the 5H-*s*-triazolo-[1,5-*b*]-*s*-triazole system (**3**); and the 1,5H-*s*-triazolo[*a*]-*s*-triazole system (**4**). In continuation of our interest in the chemistry of bridgehead nitrogen ring systems, particularly those containing an *s*-triazole nucleus,[2a,b] we have studied the ring systems **1** and **2** and in this communication describe the ready synthesis of derivatives of **1** from simple, aliphatic precursors and report the preparation of the parent ring system for the first time (Scheme I). Ring system **3** is as yet unknown but representatives of **4** have been described.[2c]

Ring closure of 4,5-diamino-3-substituted *s*-triazoles with acid anhydrides has been used[3] recently to prepare several alkyl- and aryl-substituted derivatives of ring system **1** and another recent unambiguous synthesis involved the thermal decomposition of 3-azido-4-benzylideneamino-*s*-triazoles to 6-aryl-5(7)H-*s*-triazolo-[5,1-*c*]-*s*-triazoles.[4] Other methods of synthesis have always contained an element of ambiguity in the structure of the product formed, depending on the nitrogen atom of the *s*-triazole nucleus at which ring closure occurred.

Dehydrogenative ring closures of suitably substituted amidines with lead tetraacetate have been effective in the syntheses of various alkyl- and aryl-substituted heterocycles, such as the 2-methyl- and 2-phenyl-*s*-triazolo[1,5-*a*]pyridines[5] and analogously substituted *s*-triazolo[1,5-*a*]pyrazines.[6] Ring closures between a carbon and a nitrogen or oxygen atom have also been successful under these reaction conditions.

It has now been found that the lead tetraacetate dehydrogenative ring closure of 3-benzylidenehydrazino-5-phenyl-*s*-triazole[7] (**5**, R = R′ = Ph) gives exclusively 3,6-diphenyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = R′ = Ph), which is also obtained by the action of benzoyl chloride on 4,5-diamino-3-phenyl-*s*-triazole.[3,8] Thus, in the lead tetraacetate oxidation, ring closure occurred at the 2-nitrogen atom, in preference to the 4-nitrogen atom, and it is possible that an intermediate such as **5a** was involved in the reaction. Intermediates of this type have been suggested as being of importance in the decomposition of lead tetraacetate by organic acids[9] and in the decarboxylation of diphenic acid by lead tetraacetate.[10] This reaction procedure was satisfactory for the preparation of 3-phenyl- and 3-phenyl-6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole, but no ring closure occurred with 4-amino-3-benzylidenehydrazino-*s*-triazole or its dibenzylidene derivative. The dark-brown residues obtained in these cases were most likely mixtures of azo and hydroazo compounds formed by oxidation of the amino group and it appears that the dehydrogenative ring closure is not sufficiently selective in the presence of other oxidizable groups. Attempts to cyclize 3-guanidino-5-phenyl-*s*-triazole with lead tetraacetate were also unsuccessful.

Cyanogen bromide is now well established as a cyclization agent in the formation of amino-substituted heterocyclic systems.[11-14] In the present investigation this method was found particularly successful for the synthesis of 3-amino-5(7)H-*s*-triazolo[5,1-*c*]-*s*-triazoles. Two different cyclization products can result from the reaction of cyanogen bromide with a 3-hydrazino-*s*-triazole, depending on the nitrogen atom at which ring closure occurs. In boiling methanol or dilute hydrochloric acid solution, the hydrazine hydrochlorides (**6**, R = H, CH_3, and Ph) and cyanogen bromide gave only one product, the appropriate 3-amino-6-substituted 5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = H, CH_3, and Ph; R′ = NH_2). However, in aqueous methanol at room temperature, when R = Ph, the product formed was 3-amino-5-phenyl-7H-*s*-triazolo-[3,4-*c*]-*s*-triazole (**2**, R = Ph; R′ = NH_2); when

(1) (a) Partial support of this work from USPHS Research Grant CA-05973, National Cancer Institute, and Atomic Energy Commission Contract At-(40-1)-3016 is gratefully acknowledged; (b) presented at the Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., Oct 1966; (c) abstracted from the Ph.D. dissertation (C.H.) submitted in partial fulfillment of the requirements for the Ph.D. degree, University of Louisville, June 1965; (d) to whom correspondence should be addressed at the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y. 12181.

(2) (a) K. T. Potts, H. R. Burton, T. H. Crawford, and S. W. Thomas, *J. Org. Chem.*, **31**, 3522 (1966), and earlier references listed therein. (b) K. T. Potts and R. M. Huseby, *ibid.*, **31**, 3528 (1966). (c) J. R. Bailey and N. H. Moore, *J. Am. Chem. Soc.*, **39**, 286 (1917); J. Miyatake, *J. Pharm. Soc. Japan*, **73**, 460 (1953); K. T. Potts and D. Czernikowski, unpublished results.

(3) H. Gehlen and G. Robisch, *Ann.*, **660**, 148 (1962); see also R. G. Child and A. S. Tomcufcik, *J. Heterocyclic Chem.*, **2**, 302 (1965).

(4) H. H. Takimoto, G. C. Denault, and S. Hotta, *J. Org. Chem.*, **30**, 711 (1965); *J. Heterocyclic Chem.*, **3**, 119 (1966).

(5) J. D. Bower and G. R. Ramage, *J. Chem. Soc.*, 4506 (1957); K. T. Potts, J. Bhattacharyya, and H. R. Burton, *J. Org. Chem.*, **31**, 260 (1966).

(6) G. M. Badger, P. J. Nelson, and K. T. Potts, *ibid.*, **29**, 2542 (1964).

(7) J. D. Bower and F. P. Doyle, *J. Chem. Soc.*, 727 (1957).

(8) E. Hoggarth, *ibid.*, 614 (1950).

(9) W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953).

(10) W. R. Moore and H. Arzonmanian, *J. Org. Chem.*, **27**, 4667 (1962).

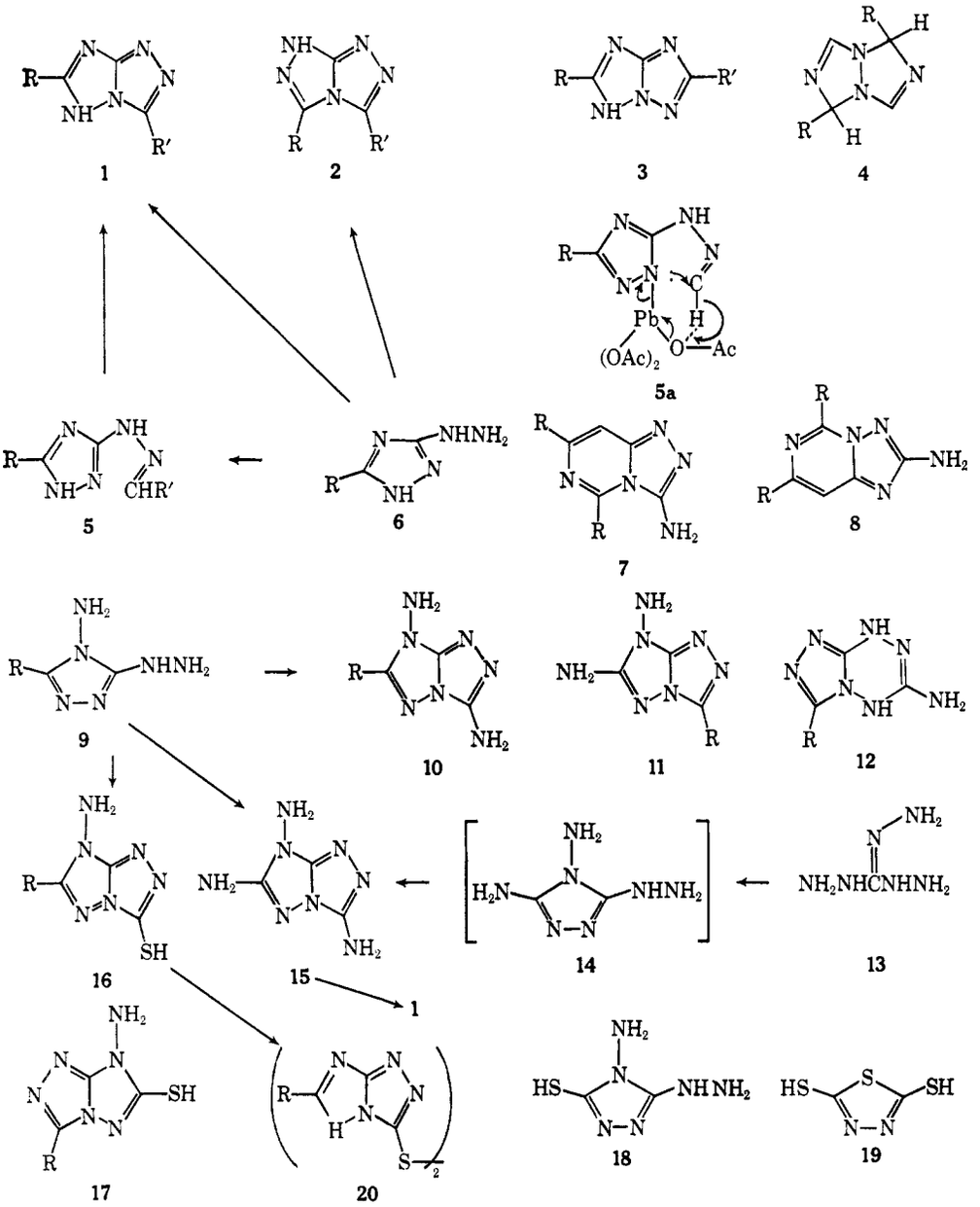
(11) G. Pellizzari, *Gazz. Chim. Ital.*, **48** (II), 151 (1918).

(12) K. T. Potts and H. R. Burton, *J. Org. Chem.*, **31**, 251 (1966).

(13) G. W. Miller and F. L. Rose, *J. Chem. Soc.*, 5642 (1963); N. K. Baser and F. L. Rose, *ibid.*, 5660 (1963).

(14) K. T. Potts and R. M. Huseby, *Chem. Ind. (London)*, 1919 (1964); *J. Org. Chem.*, **31**, 3528 (1966).

SCHEME I



R = CH_3, the product was an approximately equal mixture of the two isomers (**1**, R = CH_3; R′ = NH_2; and **2**, R = CH_3; R′ = NH_2); and when R = H, 3-amino-7H-*s*-triazolo[3,4-*c*]-*s*-triazole (**2**, R = H; R′ = NH_2) was formed in greater amount. In the presence of 2 equiv of aqueous potassium acetate solution at room temperature, **2** was the major product when R = H or CH_3 in the hydrazine (**6**); when R = Ph only an unidentifiable brown residue was obtained. Similar residues resulted in all cases when the reaction was attempted in the presence of potassium carbonate.

The assignment of the above structures was made on the basis of the following evidence. Analytical data supported the assigned molecular formulas and the absence of any absorption in the 2600–2210-cm^{-1} region in their infrared spectra eliminated the possibility of the products being intermediate cyanohydrazines. The products formed benzylidine derivatives and the differences in their melting points and infrared and ultraviolet spectra clearly established that they were different substances (see Experimental Section).

The most conclusive evidence that isomeric ring systems were involved came initially from a study of their ultraviolet absorption spectral data. The [5,1-*c*] isomers (**1**) absorbed at shorter wavelengths, but with relatively higher intensities than the [3,4-*c*] isomers (**2**). This trend has been observed previously with the isomeric *s*-triazolo[4,3-*c*]pyrimidines (**7**) and the isomeric *s*-triazolo[5,1-*c*]pyrimidines[13] (**8**) and similar relationships in the ultraviolet absorption spectra of the isomeric *s*-triazolopyridines[15] and the *s*-triazolopyrazines[6] have also been described.

Further support for the assigned structures was obtained from an investigation of the products isolated from the reaction of cyanogen bromide with 4-amino-3-hydrazino-*s*-triazole dihydrochloride (**9**) and its 5-methyl derivative. These substituted triazole derivatives were readily available[16] from triaminoguanidine and formic and acetic acids, respectively. Depending on the particular intermediate formed and the direction of

(15) H. R. Burton, Ph.D. Thesis, University of Louisville, 1963.
(16) C. F. Kroger, G. Etzold, and H. Beyer, *Ann.*, **664**, 146 (1963).

the ring closure, three products are possible: a 3,7-diamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole (**10**), a 6,7-diamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole (**11**), and the improbable product **12**. In each case only product **10** (R = H, CH_3) was obtained. Structure **12** was immediately eliminated by the products **10** (R = H, CH_3) giving dibenzylidene derivatives. Partial deamination of these diamino compounds with 1 equiv of sodium nitrite resulted in selective removal of the N-amino group. When R = H, the partial deamination product was identical with the high-melting amino compound (**1**, R = NH_2; R′ = H) obtained from the reaction of 3-hydrazino-*s*-triazole with cyanogen bromide. Analogous results were obtained with the corresponding methyl-substituted product. This interrelationship is only possible on the basis of the assigned formulas, as structure **2** cannot be obtained by partial deamination of **10** or **11** and structure **1** can only be obtained from **10** and not **11**.

The above reaction provides a convenient route to this ring system and, as the 4-amino-3-hydrazino-*s*-triazoles were prepared from triaminoguanidine, the reaction of this base with cyanogen bromide suggested a more direct route to the fused ring system. With 2 moles of cyanogen bromide, triaminoguanidine (**13**) gave a good yield of 3,6,7-triamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole (**15**). A 4,5-diamino-3-hydrazino-*s*-triazole (**14**) was most likely involved as an intermediate, but attempts to isolate this from the reaction system were unsuccessful. The variety of reaction conditions employed and the isolation of **15**, even with a large excess of **13**, indicate that the intermediate hydrazine was very susceptible to reaction with cyanogen bromide. The ultraviolet absorption spectrum of the product indicated that it belonged to the [5,1-*c*] system (Table I) and this was confirmed by deamination to 5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = R′ = H). Further confirmation of these structural assignments was obtained by a study of the products described below.

The reaction of 2-hydrazinopyridines with carbon disulfide is a particularly effective way of obtaining the *s*-triazolo[4,3-*a*]pyridine-3-thiols[12] and an interesting variation of this type of condensation is the formation of *s*-triazolo[3,4-*b*][1,3,4]thiadiazole-3-thiols from 4-amino-*s*-triazole-3-thiols and carbon disulfide.[14] In this present study, application of this reaction to the 3-hydrazino-*s*-triazoles (**6**) gave 5(7)H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiols (**1**, R = H, CH_3, and Ph; R′ = SH) without the formation of the isomeric [3,4-*c*] ring system. Owing to the instability of the hydrazines, they were used as their salts and the reaction was greatly facilitated by the addition of 1 extra equiv of base. It is most likely that the base effects removal of the proton from the β-nitrogen atom of the intermediate dithiocarbazic acid to enhance the final ring closure, as well as serving to prevent salt formation between the original hydrazine and the intermediate ditthiocarbazic acid.

The structures of these products were established from the following interrelationships. 4-Amino-3-hydrazino-*s*-triazole (**9**, R = H) was treated with carbon disulfide under reaction conditions similar to those used above and yielded a product forming a monobenzylidene derivative. This ring closure could occur in three ways, but only structures **16** and **17** need be considered. Deamination of the above reaction product gave the same product that was obtained from 3-hydrazino-*s*-triazole and carbon disulfide. This can only result from structure **16**. Analogous results were obtained for the methyl-substituted products and, though the corresponding 7-amino-6-phenyl-7H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol was not available for deamination studies, spectral characteristics indicate that the product obtained from 3-hydrazino-5-phenyl-*s*-triazole and carbon disulfide is best represented as 6-phenyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (**1**, R = Ph; R′ = SH). The thiols described above were conveniently characterized by conversion into their methylthio derivatives (see Experimental Section).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRAL DATA FOR SOME 5(7)H-*s*-TRIAZOLO[5,1-*c*]-*s*-TRIAZOLE DERIVATIVES

R	R′	Position 7	$\lambda_{max}^{CH_3OH}$, mμ (log ε)
H	H		227 (3.64); 239[a] (3.77)
H	CH_3		223 (3.69); 233[a] (3.71)
H	Ph		247 (4.18); 251[a] (4.13), 234 (4.05)[b]
Ph	H		300 (3.54),[b] 268 (4.12); 292[a] (4.22)
Ph	CH_3		302 (3.39),[b] 269 (4.04); 293[a] (4.08)
Ph	Ph		303 (3.56),[b] 254 (4.44); 292[a] (4.24), 272 (4.27),[b] 259 (5.34), 234 (4.18)[b]
NH_2			239 (4.13); 245[c] (4.12)
NH_2	CH_3		236 (3.81); 242[c] (3.89)
NH_2	Ph		248 (4.48); 280[c] (3.88),[b] 245 (4.48)
NH_2		NH_2[d]	243 (3.51); 247[c] (3.75)
NH_2	CH_3	NH_2[d]	236 (3.62); 243[c] (3.85)
NH_2	NH_2	NH_2[d]	<200; 231[c] (4.06)
SH			283 (4.14), 233 (3.73); 284[a] (4.10), 237 (3.71)
SH	CH_3		280 (4.18), 232 (3.64); 282[a] (4.18), 238 (3.74)
SH	Ph		306 (3.71), 250 (4.39); 306[a] (3.67), 250 (4.39)
SH		NH_2[d]	278 (3.95), 230 (3.70); 279[c] (4.04), 232 (3.65); 260[a] (3.77)
SH	CH_3	NH_2[d]	282 (4.18), 231 (3.66); 282[c] (4.19), 232 (3.62); 277[a] (3.98), 232 (3.81)
SH		N=CHPh	324 (4.28), 264 (4.23); 340[a] (4.10), 267 (4.25)
SCH_3			249 (3.69); 258[a] (3.84)
SCH_3		NH_2	255 (3.77); 250[c] (3.70)
SCH_3	CH_3	NH_2	253 (3.84); 270 (3.45),[b] 246 (3.73)
SCH_3	Ph		249 (4.52); 252[a] (4.49)

[a] Anion. [b] Shoulder. [c] Cation. [d] Determined in water.

It was of interest in connection with the above studies to examine the reaction of carbon disulfide with triaminoguanidine. In the presence of 2 or 3 equiv of base, 3-hydrazino-4-amino-*s*-triazole-5-thiol (**18**) was obtained, along with larger amounts of 1,3,4-thiadiazole-2,5-dithiol (**19**). The latter was characterized as its di(methylthio) ether. The dithiol probably resulted from the reaction of carbon disulfide with hydrazine, which could be formed by the hydrolysis of triaminoguanidine. It was found that **19** was readily formed in this fashion, thus confirming an earlier report[17] of its preparation from hydrazine sulfate and carbon disulfide. 3-Hydrazino-4-amino-*s*-triazole-5-thiol (**18**) has previously been prepared[18] as one of several products from the reaction of N,N¹-dithiocarbamylhydrazine with hydrazine. Though the melting point of **18** prepared in this study and also that of its dibenzylidene deriva-

(17) M. Busch, *Ber.*, **27**, 2507 (1894).
(18) C. Hoggarth, *J. Chem. Soc.*, 4817 (1952).

tive were consistently 10° higher than the literature values, all the evidence indicated that the structural assignment was correct.

Deamination Reactions of 3-Amino-5(7)H-*s*-triazolo[5,1-*c*]-*s*-triazoles.—Hypophosphorous acid was found to be particularly effective for the removal of both C- and N-amino groups after diazotization in this present study and an N-amino group could be removed selectively in the presence of a C-amino group by the use of only 1 equiv of nitrous acid. Dilute hydrochloric acid was found to be very convenient for the diazotization of N-amino groups, but when applied to C-amino groups intractable orange-brown residues were obtained. This was evidently due to the instability of the C-diazonium chloride and its susceptibility to form chloro or hydroxy compounds, a characteristic of diazonium salts of the *s*-triazole series. However, this was avoided when sulfuric acid was used in the diazotization procedure and the deaminated product was obtained in high yield.

An N-amino group was removed readily *via* the diazotization procedure, even in the absence of hypophosphorous acid. However, with a thiol group present in the molecule, as in 7-amino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (**16**, R = H), simultaneous oxidation of the deaminated thiol to the disulfide (**20**, R = H) occurred and it was necessary to add hypophosphorous acid to reduce the disulfide to the thiol (**1**, R = H; R′ = SH). This ready oxidation of the thiol (**1**, R = H; R′ = SH) to the disulfide (**20**, R = H) could be effected with nitrous acid or hydrogen peroxide and analogous results were obtained in the methyl-substituted series.

This deamination procedure which results in over 80% yield, represents an important route to 5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiols, owing to the ready accessibility of the starting materials. The lengthy syntheses of 3-hydrazino-*s*-triazoles further add to the attractiveness of the deamination route.

Deamination of 3,7-diamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazoles (**10**, R = H, CH_3) was carried out in two stages: partial deamination of **10** (R = H) afforded 3-amino-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = H; R′ = NH_2), which was deaminated to 5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = R′ = H). With 2–4 moles of sodium nitrite, both amino groups of **10** were removed at once. These reactions provide a ready synthesis of the hitherto unknown parent ring system. Deamination of **10** (R = CH_3) with excess nitrous acid gave 6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = CH_3; R′ = H) and provided a reference product that was related to one assigned the same structure and synthesized in an unambiguous fashion[3] from 3,4-diamino-*s*-triazole and acetic anhydride.

3,6,7-Triamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole (**15**), on complete deamination, gave 5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = R′ = H), clearly establishing the structure of this triaminoguanidine–cyanogen bromide reaction product. Partial deamination of **15** could not be carried out satisfactorily, product mixtures being obtained. This deamination of **15** presents the most convenient and direct route to the parent ring system.

Desulfurization Reactions of 5(7)H-*s*-Triazolo[5,1-*c*]-*s*-triazole-3-thiols.—Standard procedures for the removal of thiol groups from various *s*-triazole-3-thiols have involved the use of nitric acid[19] or Raney nickel,[19] but these procedures were unsuccessful in this present work. However, a method[20] using hydrogen peroxide as the desulfurization agent was found to be quite effective. 5H-*s*-Triazolo[5,1-*c*]-*s*-triazole-3-thiols (**1**, R = H, CH_3, Ph; R′ = SH) with hydrogen peroxide in acid solution gave only the corresponding disulfides (**20**). However, the same reaction system in the presence of barium chloride[20] gave the 5H-*s*-triazolo[5,1-*c*]-*s*-triazoles in about 50% yields. In alkaline media the desulfurization reaction was found to be much more efficient, the desired products being obtained in yields of 60–80% on decomposition of the intermediate sulfinic acids. The products (**1**, R = H, CH_3) obtained by this desulfurization procedure were identical in all respects with the corresponding products obtained by the deamination method.

Ultraviolet Absorption Spectra.—The characteristic ultraviolet absorption spectral data for this fused ring system are of interest and are briefly described here. The validity of comparing the spectral characteristics of a 10-π-electron system such as **1** to naphthalene or the indenyl anion is doubtful even though this approach has been used previously with azaindolizines[21] and various azaindoles and benzimidazoles.[22] Though the spectra of the 5(7)H-*s*-triazolo[5,1-*c*]-*s*-triazoles do resemble the spectra of various polyazaindoles, this discussion is restricted to the parent ring system and the effect of substituents on the absorption pattern.

A significant feature of the ultraviolet absorption spectra of five-membered heteroaromatic systems is the absence of bands due to n $\rightarrow$ π^* transitions. In these ring systems, with an average of 1.2 π electrons per ring atom, such transitions would be of high energy and probably hidden by $\pi \rightarrow \pi^*$ transitions. In 5(7)H-*s*-triazolo[5,1-*c*]-*s*-triazole only one absorption band at 227 mμ (log ϵ 3.64) (Table I) is observed. In water, the absorption maximum shifted to 224 mμ and in dilute acid it was further displaced to 222 mμ. Introduction of a 6-methyl substituent resulted in a hypsochromic displacement of 4 mμ, with a practically negligible change in intensity, as would be expected for alkyl substitution at a carbon atom α to an unsaturated nitrogen atom. A phenyl group in the 6 position resulted in a large bathochromic displacement of the main absorption band to 247 mμ with a significant increase in intensity. With a 3-phenyl substituent this effect is even more pronounced with the absorption shifting to 268 mμ and the appearance of a band of lower intensity as a shoulder at 300 mμ. It can be seen from Table I that this effect is constant, occurring in 6-methyl-3-phenyl- and 3,6-diphenyl-*s*-triazolo[5,1-*c*]-*s*-triazole. The lower intensity band may be due to an n $\rightarrow$ π^* transition, as the extended conjugation of the π system with the phenyl group may effectively decrease the average π-electron density per ring atom, thereby shifting the n $\rightarrow$ π^* transition to longer wavelength where it occurs as a shoulder on the long wavelength side of the main band. This shoulder is not observed in basic media, as the main absorption band undergoes a further shift to 292 mμ owing to the more extensive

(19) C. Ainsworth and R. C. Jones, *J. Am. Chem. Soc.*, **75**, 4915 (1953).

(20) J. M. Sprague and A. H. Land, "Heterocyclic Compounds," Vol. V, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p 484.

(21) S. F. Mason, "Physical Methods in Heterocyclic Chemistry," Vol. II, A. R. Katritzky, Ed., Academic Press Inc., New York, N. Y., 1963, p 59.

(22) G. Leandri, A. Mangini, and F. Montanari, *Gazz. Chim. Ital.*, **85**, 769 (1955).

π-electron delocalization in the conjugate base of the system.

The effect of introducing other substituents into the 3 position of the parent nucleus can be seen from Table I. From these data it appears that there is very little delocalization of the lone pair electrons of the amino substituent throughout both rings of the fused system. That the absorptions result from $\pi \rightarrow \pi^*$ transitions and not $n \rightarrow \pi^*$ transitions is evident from the intensities observed and from the bathochromic shifts in acid media. These shifts are in qualitative agreement with those observed[23] in similarly substituted pyridine derivatives.

The spectral data for the 5(7)H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiols (Table I) are distinctive in this series in that two almost equally intense bands are observed. The high energy band in the 230–260-mμ range is considered to be the main band of the parent nucleus shifted to longer wavelength by the substituent. The lower energy band in the 280–300-mμ region cannot be described as an $n \rightarrow \pi^*$ transition because of its relatively high intensity and insensitivity to acid and basic media. The absorption patterns of the methyl thioethers (Table I) of these thiols are distinctly different from their precursors. With the exception of 7-amino-6-methyl-3-methylthio-7H-*s*-triazolo[5,1-*c*]-*s*-triazole, these derivatives showed only one absorption band of moderate intensity and shifted to longer wavelength than for the parent nucleus. This indicated that the thiols exist predominately in solution in the thione form, though the spectrum of the presently unavailable 2-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazol-3-thione will be necessary to verify this deduction. Data for several representative infrared spectra are reported in the Experimental Section. All others were consistent with the assigned structures.

Experimental Section[24]

Dehydrogenative Ring Closure of 3-Benzylidenehydrazino-*s*-triazoles. The Preparation of 3-Phenyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (1, R = H; R′ = Ph).—This preparation illustrates the general procedure used. Lead tetraacetate (4.7 g, 0.01 mole) was added to a solution of 3-benzylidenehydrazino-*s*-triazole (2.0 g, 0.011 mole) in glacial acetic acid (10 ml). The mixture was warmed intermittently for 30 min and then heated to 80° for 15 min. After cooling, the solution was diluted with water (50 ml) and the tan solid that separated was collected, 1.5 g (76%). It crystallized from ethanol–water as colorless needles: mp 268°; infrared (cm^{-1}), main bands at 3039, 1612, 1501, 1246, 1189, 1068, 1035, 1016, 971, 917, 833, 741, 725, 680 (Table II).

Similarly, 3-phenyl-6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (1 R = CH_3; R′ = Ph) was obtained from 3-benzylidenehydrazino-5-methyl-*s*-triazole (5, R = CH_3; R′ = Ph) and 3,6-diphenyl-5H-*s*-triazolo[5,1-*c*]*s*-triazole (1, R = R′ = Ph) from 3-benzylidenehydrazino-5-phenyl-*s*-triazole (5, R = R′ = Ph) (Table II).

Reaction of Cyanogen Bromide with 3-Hydrazino-*s*-triazoles. 3-Amino-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (1, R = H; R′ = NH_2).—This preparation illustrates the general procedure employed. A solution of 3-hydrazino-*s*-triazole hydrochloride[25] (10.0 g, 0.074 mole) and cyanogen bromide (7.8 g, 0.074 mole) in aqueous methanol (300 ml, 85%) was refluxed for 48 hr. The solvent was removed by evaporation, the solid residue was dissolved in water (25 ml), and when the solution was neutralized with potassium acetate a pale yellow solid precipitated. The product crystallized from water as colorless prisms: 6.2 g (67%); mp 260°; infrared (cm^{-1}) main bands at 3184, 3105, 1650, 1623, 1592, 1250, 1179, 1160, 1033, 900, 854, 793, 735, 719, 700, 657 (Table II).

The benzylidene derivative was prepared by refluxing equimolar amounts of the amino compound and benzaldehyde in aqueous alcohol with a trace of potassium carbonate. It crystallized from ethanol as colorless needles: mp 264°; infrared (cm^{-1}) main bands at 3030, 1605, 1428, 1351, 1220, 1183, 971, 926, 892, 769, 740, 709, 633 (Table II).

The following were prepared from the appropriate starting material listed and are described in Table II.

3-Amino-6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (1, R = CH_3; R′ = NH_2) was obtained from 3-hydrazino-5-methyl-*s*-triazole hydrochloride:[26] infrared (cm^{-1}) main bands at 3267, 3086, 1672, 1639, 1602, 1326, 1265, 1190, 1152, 1037, 990, 826, 685, 662.

3-Amino-6-phenyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (1, R = Ph; R′ = NH_2) was obtained from 3-hydrazino-5-phenyl-*s*-triazole hydrochloride:[27] infrared (cm^{-1}) main bands at 3225, 3086, 1642, 1620, 1594, 1501, 1338, 1282, 1187, 1111, 1075, 1024, 934, 787, 746, 699. 3,7-Diamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole hydrochloride (10, R = H) was obtained from 4-amino-3-hydrazino-*s*-triazole dihydrochloride (9, R = H).[16] The free base was obtained by dissolving the hydrochloride in water and neutralizing with potassium acetate. The diamino compound crystallized from water as dense, irregular prisms: mp 223°; infrared (cm^{-1}) main bands at 3144, 2994, 1639, 1623, 1589, 1529, 1430, 1233, 1216, 1114, 1079, 1004, 962, 909, 752.

3,7-Dibenzylideneamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole was prepared from the above diamino compound (1.4 g, 0.01 mole) in dilute acetic acid (50 ml) containing benzaldehyde (3 ml, 0.03 mole) under reflux (2 hr). After addition of water (100 ml), a yellow solid separated and was recrystallized from dimethylformamide–water forming pale yellow needles: mp 229–230°; infrared (cm^{-1}) main bands at 1602, 1555, 1510, 1338, 1288, 1240, 1225, 1170, 1016, 780, 690.

3,7-Diamino-6-methyl-7H-*s*-triazolo[5,1-*c*]-*s*-triazole (10, R = CH_3) was obtained fro m 3-hydrazino-4-amino-5-methyl-*s*-triazole hydrochloride (9, R = CH_3).[16] Its dibenzylideneamino derivative was prepared as described above and separated from dimethylformamide–water as pale yellow needles, mp 235°.

3-Amino-7H-*s*-triazolo[3,4-*c*]-*s*-triazole (2, R = H; R′ = NH_2).—A solution of 3-hydrazino-*s*-triazole hydrochloride (3.0 g, 0.022 mole) and cyanogen bromide (2.4 g, 0.022 mole) in aqueous methanol (75 ml, 85%) was allowed to stand at room temperature for 4 days. The solvent was then removed, the residue was dissolved in water (15 ml), and the resulting acid solution was neutralized with potassium acetate. Over a period of 2 hr a tan solid separated. It was recrystallized from water and separated as colorless needles: yield, 1.5 g (60%); mp 205° dec; infrared (cm^{-1}) main bands at 3225, 2985, 1655, 1623, 1587, 1204, 1177, 1156, 1023, 990, 961, 892, 862, 793, 730, 690; $\lambda_{max}^{CH_3OH}$ 246 mμ (log ϵ 3.72).

Anal. Calcd for $C_3H_4N_6$: C, 29.0; H, 3.25; N, 67.7. Found: C, 29.0; H, 3.2; N, 67.8.

The same product was obtained when the reaction was carried out in the presence of potassium acetate, but with potassium carbonate an intractable product only was obtained.

3-Amino-5-methyl-7H-*s*-triazolol[3,4-*c*]-*s*-triazole (2, R = CH_3; R′ = NH_2).—The above procedure was used with 3-hydrazino-5-methyl-*s*-triazole hydrochloride (3.0 g, 0.02 mole) with the following modifications. After the solvent was removed, the residue was treated with absolute ethanol (50 ml) and the undissolved white solid was collected and saved. The filtrate was diluted with ether (300 ml) and the pale yellow solid which separated was collected and dissolved in water (10 ml). Neutralization of the resulting acid solution with potassium acetate precipitated a white solid that crystallized from water as colorless needles: yield, 0.5 g (17%); mp 265°. A mixture melting point with a sample of 3-amino-6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole was not depressed and the infrared absorption spectra of the two samples were identical.

(23) See ref 21, p 41.

(24) All evaporations were done under reduced pressure using a Rotavap apparatus. Melting points were determined in capillaries and infrared spectra were measured in KBr pellets on a Baird IR2 or a Perkin-Elmer 421 spectrophotometer unless otherwise mentioned. The ultraviolet absorption data were obtained using a Beckman DK2 spectrophotometer and microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

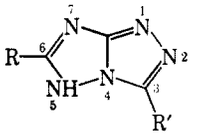
(25) W. Manchot and R. Noll, *Ann.*, **343**, 1 (1905).

(26) E. Lieber, S. Shiff, A. Henry, and W. G. Finnegan, *J. Org. Chem.*, **18**, 218 (1953).

(27) W. Manchot, *Ber.*, **43**, 1316 (1910).

TABLE II

SOME DERIVATIVES OF THE 5(7)H-*s*-TRIAZOLO[5,1-*c*]-*s*-TRIAZOLE SERIES



Substituents				Yield,				Calcd, %			Found, %		
R′	R	Position 7	Mp, °C	%	Solvent[j]	Habit[a]	Formula	C	H	N	C	H	N
Ph	H		268	76	E-W	*b*	$C_9H_7N_5$	58.4	3.8	37.8	58.4	3.9	37.9
Ph	CH_3		255	50	E-W	*b*	$C_{10}H_9N_5$	60.3	4.55	35.2	60.2	4.65	35.2
Ph	Ph		260[c]	75	E	*b*							
NH_2	H		260	67	W	*d*	$C_3H_4N_6$	29.0	3.25	67.7	28.9	3.25	67.9
PhCH=N	H		264	...	E	*b*	$C_{10}H_8N_6$	56.6	3.8	39.6	56.4	3.9	39.4
NH_2	CH_3		265	54	W	*b*	$C_4H_6N_6$	34.8	4.4	60.8	34.9	4.25	60.6
NH_2	Ph		270	52	E-W	*d*	$C_9H_8N_6$	54.0	4.0	42.0	54.1	4.3	42.25
NH_2	H	NH_2	255[e]	75	E	*f*	$C_3H_6ClN_7$	20.6	3.4	56.0	20.5	3.5	55.75
NH_2	H	NH_2	223	...	W	*d*	$C_3H_5N_7$	25.9	3.6	70.5	25.8	3.4	70.7
PhCH=N	H	PhCH=N	229–230	...	DMF-W	*g*	$C_{17}H_{13}N_7$	64.8	4.1	31.1	65.1	4.2	31.2
NH_2	CH_3	NH_2	291	30	W	*d*	$C_4H_7N_7$	31.4	4.6	64.0	31.6	4.5	63.8
PhCH=N	CH_3	PhCH=N	235	...	DMF-W	*g*	$C_{18}H_{15}N_7$	65.6	4.6	29.8	65.4	4.45	29.8
NH_2	NH_2	NH_2	295[e]	80	*h*	*f*	$C_3H_7ClN_8$	18.9	3.7	58.8	18.9	3.8	58.5
NH_2	NH_2	NH_2	250 dec	...	W	*d*	$C_3H_6N_8$	23.4	3.9	72.7	23.3	4.0	72.8
SH	H		237	53	W	*d*	$C_3H_3N_5S$	25.5	2.1	49.6	25.3	2.15	49.7
SH	CH_3		248	45	W	*b*	$C_4H_5N_5S$	31.0	3.2	45.2	30.9	3.3	45.4
SH	Ph		240	75	E	*d*	$C_9H_7N_5S$	49.8	3.25	32.25	49.85	3.5	32.5
SH	H	NH_2	203	80	W	*b*	$C_3H_4N_6S$	23.1	2.6	53.8	23.0	2.7	53.7
SH	H	PhCH=N	253	...	DMF-W	*g*	$C_{10}H_8N_6S$	49.2	3.3	34.4	49.5	3.3	34.2
SH	CH_3	NH_2	227	36	W	*b*	$C_4H_6N_6S$	28.2	3.5	49.4	28.3	3.6	49.2
SH	CH_3	PhCH=N	265	...	DMF-W	*g*	$C_{11}H_{10}N_6S$	51.2	3.9	32.6	51.0	4.1	32.6
CH_3S	H		195	65	E-B	*f*	$C_4H_5N_5S$	31.0	3.2	45.2	31.1	3.3	45.4
CH_3S	H	NH_2	200	87	E-B	*f*	$C_4H_6N_6S$	28.2	3.5	49.4	28.45	3.8	49.6
CH_3S	CH_3	NH_2	185	30	E	*d*	$C_5H_8N_6S$	32.6	4.35	45.65	32.5	4.2	45.5
CH_3S	Ph		228	30	E	*f*	$C_{10}H_9N_5S$	51.9	3.9	30.3	51.7	3.75	30.1
H	H		250	42	E(W)	*b*	$C_3H_3N_5$	33.0	2.75	64.2	33.2	3.0	64.1
H	CH_3		235[i]	33	E(W)	*d*	$C_4H_5N_5$	39.0	4.1	56.9	39.3	4.3	57.0
H		NH_2	225	18	E	*f*	$C_3H_4N_6$	29.0	3.25	67.7	29.05	3.2	67.95
H	Ph		215	50	E-W	*b*	$C_9H_7N_5$	58.4	3.8	37.8	58.2	3.6	37.6

[a] All colorless except where noted. [b] Needles. [c] Lit.[3,7,8] mp 268°, 266°, 257°, respectively. [d] Irregular prisms. [e] Hydrochloride. [f] Platelets. [g] Pale yellow needles. [h] Dilute hydrochloric acid. [i] Lit.[3] mp 236°. [j] B = benzene; E = ethanol; DMF = dimethylformamide; W = water.

The insoluble material from above was dissolved in water (20 ml) and the resulting acid solution was neutralized with potassium acetate. Over a period of 1 hr 3-amino-5-methyl-7H-*s*-triazolo[3,4-*c*]-*s*-triazole separated and crystallized from water as colorless needles: yield, 1.2 g (43%); mp 210° dec; infrared (cm^{-1}) main bands at 3225, 3012, 1666, 1631, 1592, 1351, 1133, 1018, 877, 869, 699; $\lambda_{max}^{CH_3OH}$ 250 mμ (log ε 3.78).

Anal. Calcd for $C_4H_6N_6$: C, 34.8; H, 4.4; N, 60.8. Found: C, 34.8; H, 4.6; N, 61.05.

Attempted Preparation of 3-Amino-5-phenyl-7H-*s*-triazolo[3,4-*c*]-*s*-triazole (2, R = Ph; R′ = NH_2).—From 3-hydrazino-5-phenyl-*s*-triazole hydrochloride (3.5 g, 0.015 mole) under the above reaction conditions, the only product obtained was 3-amino-6-phenyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (1, R = Ph; R′ = NH_2): yield, 1.8 g (60%); mp 270°. The mixture melting point with an authentic sample was not depressed and their infrared absorption spectra were identical.

Reaction of Triaminoguanidine with Cyanogen Bromide. 3,6,7-Triamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole (15).—Triaminoguanidine hydrochloride[16] (7.0 g, 0.05 mole) was dissolved in hydrochloric acid (1 *N*, 150 ml). Cyanogen bromide (10.6 g, 0.10 mole) was added and the solution was stirred and heated at 60° for 2 hr and then under reflux for 1 additional hr. When cooled to 0°, the solution deposited white platelets, 5.5 g (57%), of the monohydrochloride of 3,6,7-triamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole, mp 295°. Recrystallization from dilute hydrochloric acid did not raise the melting point.

The free base was obtained by neutralizing an aqueous solution of the hydrochloride with sodium carbonate. Crystallization from water gave colorless, irregular, prisms: mp 250° dec; infrared (cm^{-1}) main bands at 3205, 3086, 1658, 1618, 1577, 1547, 1508, 1404, 1295, 1243, 1108, 971, 943, 855, 704.

Use of 85% aqueous methanol as solvent in the above reaction raised the crude yield to 80%.

The triamino compound was heated in dilute acetic acid in the presence of 3 *M* quantities of benzaldehyde for 8 hr. The product crystallized from dimethylformamide–water as deep-yellow needles, mp 255°. The elemental analysis indicated that the product was a dibenzylidene monohydrate derivative of the triamino compound.

Anal. Calcd for $C_{17}H_{18}N_8O$: C, 58.6; H, 4.6; N, 32.2. Found: C, 58.85; H, 4.65; N, 32.7.

Reaction of Carbon Disulfide with 3-Hydrazino-*s*-triazoles. The Preparation of 5H-*s*-Triazolo[5,1-*c*]-*s*-triazole-3-thiol (1, R = H; R′ = SH).—This preparation illustrates the general procedure used. A solution of 3-hydrazino-*s*-triazole hydrochloride (6.4 g, 0.048 mole) and potassium hydroxide (5.4 g, 0.096 mole) in aqueous ethanol (150 ml, 70%) was refluxed with carbon disulfide (25 ml) for 30 hr. The solvent was removed by evaporation under reduced pressure and the solid residue was dissolved in water (25 ml). The resulting basic solution was acidified (pH 3) by addition of concentrated hydrochloric acid. The pale yellow solid which separated was filtered off and recrystallized from water, forming colorless prisms: yield, 4.0 g (53%); mp 237°; infrared, Nujol (cm^{-1}), main bands at 3003, 1639, 1492, 1379, 1338, 1277, 1257, 1036, 962, 935, 820, 758, 714, 704 (Table II). The other 3-thiol derivatives listed in Tables II were prepared from the appropriately substituted hydrazines described above.

Reaction of Triaminoguanidine with Carbon Disulfide.—Triaminoguanidine hydrochloride (14.0 g, 0.10 mole), carbon disulfide (20 ml), and 3 equiv of potassium hydroxide were heated under reflux for 16 hr. The reaction mixture was cooled and the white solid (2.0 g) that separated was collected. It

crystallized from a large volume of water as colorless, irregular prisms, mp 240°. This compound was identified as 3-hydrazino-4-amino-*s*-triazole-5-thiol (**18**) (lit.[18] mp 230°): infrared (cm^{-1}) main bands at 3154, 3076, 1644, 1600, 1503, 1418, 1338, 1160, 1092, 980, 952, 847, 704.

Anal. Calcd for $C_2H_6N_6S$: C, 16.4; H, 4.1; N, 57.5. Found: C, 16.4; H, 4.1; N, 56.9.

The dibenzylidene derivative was prepared by heating an acetic acid solution of the compound on a steam bath in the presence of excess benzaldehyde. The product crystallized from dimethylformamide–water as yellow needles, mp 254° (lit.[18] mp 245°).

Anal. Calcd for $C_{16}H_{14}N_6S$: C, 59.6; H, 4.4; N, 26.1. Found: C, 59.3; H, 4.6; N, 26.3.

When the original filtrate was acidified, a yellow solid separated: yield, 10.0 g; mp 165°. It crystallized from water as yellow, irregular prisms, mp 168°. A mixture melting point with an authentic sample of 1,3,4-thiadiazole-2,5-dithiol (**19**) was not depressed (lit.[17] mp 168°) and the infrared absorption spectra of the products were identical.

Anal. Calcd for $C_2H_2N_2S_3$: C, 16.0; H, 1.3. Found: C, 16.1; H, 1.45.

The di(methylthio) derivative was prepared with methyl iodide and potassium hydroxide in methanol. It crystallized from benzene as pale yellow platelets, mp 136° (lit.[28] mp 136°).

From the reaction of triaminoguanidine hydrochloride with carbon disulfide in the presence of only 2 equiv of potassium hydroxide, 1,3,4-thiadiazole-2,5-dithiol and another product were obtained. The latter, which separated directly from the reaction mixture, crystallized from water as white needles, mp 230°. It was soluble in base, insoluble in acid, and stable to hot acid or base but could not be identified: infrared (cm^{-1}) main bands at 3125, 3030, 1666, 1336, 1282, 1215, 1140, 1086, 1048, 970, 714, 640.

Synthesis of Methylthio Derivatives.—The thiols were refluxed in methanol in the presence of equimolar quantities of sodium hydroxide and methyl iodide for 1–2 hr. Partial evaporation of the solvent and dilution with water precipitated the methylthio derivatives. An alternative procedure for heat sensitive products was to shake the reactants in water in a closed container and then allow the reaction mixture to stand at room temperature overnight. These products are described in Table II.

Deamination Reactions of Amino-Substituted 5(7)H-*s*-Triazolo[5,1-*c*]-*s*-triazoles. Deamination of 7-Amino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (16, R = H). A.—A mixture of concentrated sulfuric acid (100 ml) and water (50 ml) was cooled in an ice–salt bath to −10°. Sodium nitrite (3.7 g, 0.54 mole) was added in small portions over a period of 15 min followed by dropwise addition of cold 50% hypophosphorus acid (19.3 ml, 0.19 mole). The temperature was kept below −10° and 7-amino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (3.1 g, 0.02 mole) was added in small portions with vigorous stirring. The temperature was kept at −10° for 2 hr and then the reaction mixture was warmed slowly to 60° and stirred at this temperature for another 2 hr. The mixture was then cooled to 25°, diluted with water (200 ml), and filtered. The filtrate, upon standing overnight, deposited colorless needles, 0.5 g (20%), mp 237°. A mixture melting point determination with 5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (**1**, R = H; R′ = SH) showed no depression and the infrared absorption spectra of the two products were identical.

B.—A suspension of 7-amino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (**16**, R = H) (1.7 g, 0.01 mole) in dilute hydrochloric acid (0.7 *N*, 50 ml) was cooled to −10° with vigorous stirring and a solution of sodium nitrite (0.7 g, 0.01 mole) in water (10 ml) was added dropwise. The mixture frothed and a fine precipitate formed. Stirring was continued for 1 hr at −10°. After dilution with water (100 ml), the solid was collected: yield, 0.8 g (50%). This product was identified as 5H-*s*-triazolo[5,1-*c*]-*s*-triazol-3-yl disulfide (**20**, R = H). It crystallized from a large volume of water as pale-yellow needles: mp 250°; infrared (cm^{-1}) main bands at 3048, 1602, 1383, 1273, 1242, 1190, 1165, 1102, 1075, 971, 926, 877, 826, 741, 645, 633.

Anal. Calcd for $C_6H_4N_{10}S_2$: C, 25.7; H, 1.4; N, 50.0. Found: C, 25.5; H, 1.35; N, 50.4.

An identical sample was prepared by treatment of 5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol with hydrogen peroxide.

C.—A suspension of the amino compound (1.6 g, 0.01 mole) in dilute hydrochloric acid (0.7 *N*, 50 ml) was cooled to −10°. A solution of sodium nitrite (1.4 g, 0.02 mole) in water (10 ml) was added dropwise to the suspension and the mixture was stirred for 1 hr at −10°. Hypophosphorous acid (50%, 10 ml) was added and the mixture was stirred at room temperature for 4 hr, warmed to 60°, and filtered. The filtrate was partially evaporated and the white solid was filtered off and recrystallized from water, giving 1.2 g (85%) of colorless product, mp 237°. A mixture melting point with 5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol was not depressed and the infrared absorption spectra of the two products were identical.

Deamination of 6-Methyl-7-amino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (16, R = CH_3).—Using method B, pale yellow needles (0.8 g, 46%) of 6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazol-3-yl disulfide (**20**, R = CH_3) were obtained: mp 258°; infrared (cm^{-1}) main bands at 3030, 1600, 1367, 1314, 1206, 1098, 1068, 1017, 855, 820, 725.

Anal. Calcd for $C_8H_8N_{10}S_2$: C, 31.2; H, 2.6; N, 45.45. Found: C, 30.8; H, 3.0; N, 45.1.

Using method C, a product crystallized from water as colorless needles: yield, 1.3 g (85%); mp 247°. A mixture melting point determination with 6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol was not depressed and the infrared absorption spectra of the two products were identical.

Deamination of 3,7-Diamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole (10, R = H). A. Partial Deamination.—Method C was applied to the diamino compound (0.01 mole) with the following modifications. After addition of sodium nitrite (0.01 mole) and hypophosphorous acid (10 ml), the mixture was warmed slowly to 60°. The solution was then evaporated to dryness under reduced pressure and the residue was dissolved in water (25 ml). The resulting acid solution was neutralized by addition of potassium acetate and left standing overnight. The red, crystalline solid which separated was recrystallized (Norit) from water and formed colorless, irregular prisms: yield, 0.9 g (75%); mp 260°. A mixture melting point with 3-amino-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = H; R′ = NH_2) was not depressed and the infrared spectra of the two products were identical.

B. Complete Deamination.—Using method A and 2 equiv of sodium nitrite and hypophosphorous acid, the reaction mixture was kept at −10° for 2 hr and then allowed to warm to room temperature. After standing overnight, the pale orange solution was neutralized with potassium carbonate and evaporated to dryness. The residue was extracted with four 50-ml portions of hot, absolute ethanol and the combined extracts were evaporated to dryness. This residue was continuously extracted with boiling ethyl acetate for 24 hr. Evaporation of the ethyl acetate left 0.9 g (42%) of crude 5H-*s*-triazolo[5,1-*c*]-*s*-triazole. It crystallized from ethanol or water as colorless needles: mp 250°; infrared (cm^{-1}) main bands at 3067, 1612, 1538, 1280, 1250, 1184, 1150, 1010, 970, 943, 862, 806, 746, 657.

Deamination of 3-Amino-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (1, R = H; R′ = NH_2).—From the amino compound (1.2 g, 0.01 mole) was obtained 5H-*s*-triazolo[5,1-*c*]-*s*-triazole: yield, 0.3 g (30%); mp 250°. A mixture melting point with the product obtained by complete deamination of 3,7-diamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole was not depressed and the infrared absorption spectra of the two products were identical.

Deamination of 3,7-Diamino-6-methyl-7H-*s*-triazolo[5,1-*c*]-*s*-triazole (10, R = CH_3). A. Partial Deamination.—Using the partial deamination procedure described above, the amino compound (0.01 mole) gave a product which crystallized from water as small colorless needles: yield, 0.5 g (40%); mp 265°. A mixture melting point with 3-amino-6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = CH_3; R′ = NH_2) was not depressed and the infrared absorption spectra of the two products were identical.

B. Complete Deamination.—By the above, complete deamination procedure the amino compound (0.02 mole) gave 0.8 g (33%) of crude 6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = CH_3; R′ = H). It crystallized from ethanol or water as colorless, irregular prisms: mp 235° (lit.[3] mp 236°); infrared (cm^{-1}) main bands at 2994, 1612, 1563, 1418, 1315, 1243, 1136, 1036, 990, 862, 840, 813, 746.

Deamination of 3-amino-6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole (**1**, R = CH_3; R′ = NH_2) by the above procedure gave a 33% yield of a product which was identical in every way with 6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole.

Deamination of 3,6,7-Triamino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole (15).—The complete deamination procedure was applied to this

(28) E. Ziegele, *J. Prakt. Chem.*, **202**, 60 (1899).

compound (3.1 g, 0.02 mole) in the presence of 0.08 mole of sodium nitrite. Evaporation of the ethyl acetate extract left 1.0 g (48%) of the crude product. It crystallized from ethanol or water as colorless needles, mp 250°. A mixture melting point with 5H-*s*-triazolo[5,1-*c*]-*s*-triazole was not depressed and the infrared absorption spectra were identical.

Desulfurization of 7-Amino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (16, R = H) with Hydrogen Peroxide.—A mixture of the thiol (1.6 g, 0.1 mole) and barium chloride dihydrate (2.4 g, 0.01 mole) was suspended in concentrated hydrochloric acid (12 *N*, 25 ml). The mixture was stirred and aqueous hydrogen peroxide (30%, 3.5 g, 0.03 mole) in water (10 ml) was added dropwise over a period of 10 min. After heating the solution at 80-90° for 1 hr, it was cooled and filtered to remove barium sulfate. The filtrate was neutralized and evaporated to dryness and the residue was extracted with three 50-ml portions of hot, absolute ethanol. The combined extracts were evaporated to dryness and the residue was continuously extracted with hot ethyl acetate for 48 hr. Evaporation of the extract left 0.8 g of crude 7-amino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole, mp 210–220°. Two recrystallizations from ethanol gave the amino compound as colorless platelets: yield, 0.2 g (18%); mp 225°; infrared (cm^{-1}) main bands at 3236, 3048, 1597, 1529, 1243, 1223, 1193, 1126, 1025, 980, 952, 917, 840, 826, 740, 626.

Desulfurization of 5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (1, R = H; R′ = SH) (1.4 g, 0.01 mole) by the hydrogen peroxide method gave 0.6 g (58%) of 5H-*s*-triazolo[5,1-*c*]-*s*-triazole, mp 250°. A mixture melting point with a sample prepared by deamination of 3-amino-5H-*s*-triazolo[5,1-*c*]-*s*-triazole was not depressed and the infrared absorption spectra of the two products were identical.

The residue, insoluble in ethyl acetate, was dissolved in water (25 ml). The resulting, slightly basic solution was neutralized and the pale yellow solid that separated was filtered off and recrystallized from a large volume of water, giving 0.2 g of product, mp 250°. A mixture melting point with 5H-*s*-triazolo[5,1-*c*]-*s*-triazol-3-yl disulfide was not depressed and the infrared absorption spectra of the two products were identical.

Repeating the reaction as above, except that no barium chloride was added, gave, as the only product, the disulfide: yield, 0.5 g (30%); mp 250°.

Desulfurization of 6-Methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (1, R = CH_3; R′ = SH).—The thiol (0.7 g, 0.005 mole) was dissolved in water (20 ml) containing sodium hydroixde (0.4 g, 0.01 mole). The solution was stirred and aqueous hydrogen peroxide (30%, 1.2 g, 0.01 mole) was added dropwise over a period of 10 min. After stirring the reaction mixture for 3 hr at room temperature, it was treated with concentrated sulfuric acid (20 ml) and diluted with water (75 ml). After standing overnight, the solution was neutralized (pH 7) and evaporated to dryness. The residue was extracted with three 50-ml portions of hot, absolute ethanol and the combined extracts were evaporated to dryness. The residue was extracted continuously with hot ethyl acetate for 24 hr and evaporation of the extract gave 0.4 g (66%) of crude 6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole. Crystallization from water gave colorless, irregular prisms, mp 235°. A mixture melting point with a sample prepared by deamination of 3-amino-6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole was not depressed and the infrared absorption spectra of the two products were identical.

Desulfurization of 6-phenyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (1, R = Ph; R′ = SH) (0.7 g, 0.004 mole) was carried out by the procedure described immediately above. 6-Phenyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole crystallized from ethanol–water as colorless needles: yield, 0.3 g (50%); mp 215°.

Registry No.—**1a**, 14661-17-7; **1b**, 14661-18-8; **1c**, 6388-02-9; **1d**, 13728-21-7; **1e**, 13728-22-8; **1f**, 3529-51-9; **1g**, 14661-23-5; **1h**, 14661-24-6; **1i**, 13728-18-2; **1j**, 13728-20-6; **1k**, 13728-23-9; **1l**, 14661-28-0; **1m**, 14661-29-1; **1n**, 13728-15-9; **1o**, 13728-26-2; **1p**, 14661-32-6; **1q**, 14661-33-7; **1r**, 13728-28-4; **1s**, 14661-35-9; **1t**, 14661-36-0; **1u**, 14661-37-1; **1v**, 13728-27-3; **1w**, 13728-29-5; **1x**, 14661-40-6; **1y**, 14661-41-7; **1z**, 251-93-4; **1aa**, 13728-25-1; **1bb**, 14661-44-0; **1cc**, 6219-30-3; **2** (R = H; R′ = NH_2), 14723-34-3; **2** (R = CH_3; R′ = NH_2), 14661-46-2; **18**, 1750-12-5; **20** (R = H), 14661-47-3; **20** (R = CH_3), 14661-59-7.

Acknowledgment.—The authors are indebted to Professor H. Gehlen for a sample of 6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole.

Reactions of O-Benzoyl Oximes with Sodium Hydride. Substituted Isoxazoles and the Neber Rearrangement[1]

W. B. RENFROW, J. F. WITTE, R. A. WOLF, AND W. R. BOHL

Department of Chemistry, Oberlin College, Oberlin, Ohio 44074

Received July 21, 1967

4-Benzoyl-3,5-diphenylisoxazole and a derivative of phenacylamine have been isolated from the reaction products of acetophenone O-benzoyl oxime with sodium hydride. Corresponding products were obtained from *para*-substituted acetophenone O-benzoyl oximes. Propiophenone O-benzoyl oxime, cyclohexanone O-benzoyl oxime, and acetophenone O-(2,4,6-trimethylbenzoyl) oxime gave Neber rearrangement products but no isoxazoles.

The reaction between O-benzoyl oximes and sodium hydride offers interesting possibilities for condensation and elimination reactions. Acetophenone O-benzoyl oxime (**1a**) in boiling toluene reacted smoothly with sodium hydride to evolve an approximately equimolar amount of hydrogen. The reaction mixture was treated with dilute hydrochloric acid and the organic layer subsequently extracted wih sodium carbonate solution. Acid-soluble, base-soluble, and neutral products were isolated.

The acid-soluble product polymerized when the solution was made basic, but was identified as phenacylamine hydrochloride (**2**) by conversion to the N-benzoyl derivative (**3a**). The reaction leading to this product seems properly classified as a Neber rearrangement.[2] 3-Phenyl-2H-azirine (**4**) is probably an intermediate.[3]

The base-soluble product was identified as benzoic acid.

Neutral products of the reaction included acetophenone oxime and a new[4] compound shown to be 4-benzoyl-3,5-diphenylisoxazole (**5a**). The structure of **5a** was deduced from elemental analysis, molecular weight determination, strong absorption at 6.05 μ (C=O), and

(1) Supported by National Science Foundation URP Grants G-22895 and GY-215.

(2) P. W. Neber and A. Friedoesheim, *Ann.*, **449**, 109 (1926).

(3) C. O'Brien, *Chem. Rev.*, **64**, 81 (1964); D. F. Morrow, M. E. Butler, and E. C. Y. Huang, *J. Org. Chem.*, **30**, 579 (1965).

(4) An isomer, 5-benzoyl-3,5-diphenylisoxazole, has been reported: E. P. Kohler, *J. Am. Chem. Soc.*, **47**, 3032 (1925).