ether, and dried *in vacuo* over P_2O_5. The azo derivative of **8** was isolated by evaporation of the trifluoroacetic acid solution, and washing of the resulting residue with ethanol and ether. In addition, **6** and **17** coupled with 2-naphthol in dimethyl sulfoxide to provide the azo derivative. In the reaction of **6** a precipitate was isolated that analyzed for a 1:1 complex of **6** and dimethyl sulfoxide (see Table I). All the azo derivatives were identified by the absence of a diazo absorption band in the infrared spectra, and the presence of a band near 500 mμ in the visible spectra (see Table III).

Acknowledgment.—The authors are indebted to Dr. W. C. Coburn, Jr., and Mrs. Martha C. Thorpe, for their aid in the interpretation of the pmr spectra, and to Dr. W. J. Barrett and the members of the Analytical Chemistry Division of Southern Research Institute, for the spectral and microanalytical determinations. Some of the analyses reported were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

meso Ionic Compounds. II. Derivatives of the *s*-Triazole Series

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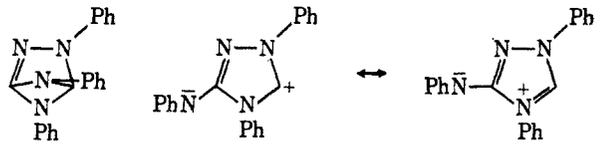
Further examples of *meso* ionic compounds containing the *s*-triazole nucleus are reported and exceptions to the cyclization procedures leading to these products are noted. These *meso* ionic compounds do not take part in 1,3-dipolar addition reactions. Convenient routes to *s*-triazolium salts are also described.

In studies of the chemistry of the *s*-triazole ring system,[2] our attention was drawn to a series of products to which unlikely structures had been assigned in the early literature. In an earlier, preliminary communication,[1c] we showed that some of these products were best regarded as *meso* ionic compounds, of which the most often quoted example is the sydnone system,[3] and we now describe further examples of these products as well as exceptions to the cyclization procedures used in their synthesis. Related ring closures leading to *s*-triazolium salts are also described.

On the basis of dipole moment data, Schonberg[4a] and Warren[4b] suggested that the bridged-ring *endo*-triazolines obtained by Busch and co-workers[5] did not exist as such but rather as zwitterions. Thus the large dipole moment (7.2 D.) of the nitric acid precipitant "nitron" (**1**) suggested a zwitterion structure, of which **2** and **3** are two possible canonical forms.



1 **2** **3**

In an early review of the sydnones, Baker and Ollis[6] suggested that these *endo*-triazolines were analogous to the sydnones and that they could be represented as *meso* ionic compounds. Our earlier work established the *meso* ionic nature of these products and showed that they belonged to the *s*-triazole system and not the alternative, isomeric 1,3,4-oxadiazole or thiadiazole ring systems. The correct skeletal arrangement of the atoms was shown by the synthesis of many of these products using ring closures at different portions of the molecule in such a way that skeletal rearrangements were precluded. This was found to be true in all cases except one, and the detailed experimental study needed to establish the behavior of this particular reaction system is described in detail below. The ring systems were also degraded to products that confirmed the assigned structures.

This was illustrated by the synthesis, among others, of *anhydro*-5-hydroxy-2,3,4-triphenyl-*s*-triazolium hydroxide (**6**, $R_1 = R_2 = R_3 = Ph$; X = O), originally represented as 2,3,4-triphenyl-3,4-endoxytriazoline (**4**, $R_1 = R_2 = R_3 = Ph$) by the action of phosgene on N-amino-N,N′-diphenylbenzamidine (**5**, $R_1 = R_2 = R_3 = Ph$), and also by the ring closure of 1-benzoyl-1,4-diphenylsemicarbazide (**7**, $R_1 = R_2 = R_3 = Ph$; X = O) with sodium ethoxide. The latter cyclization could not be effected with acidic cyclodehydration agents or by heat; with acetic acid–acetic anhydride the product isolated was shown to be 1-benzoyl-2,2-diacetyl-1-phenylhydrazine. This structure was confirmed by its synthesis using standard procedures and the formation of this product can be readily attributed to thermal decomposition of 1-benzoyl-1-phenylthiosemicarbazide to 1-benzoyl-1-phenylhydrazine followed by acetylation with acetic anhydride. The corresponding cyclization of 1-benzoyl-1,4-diphenylthiosemicarbazide (**7**, $R_1 = R_2 = R_3 = Ph$; X = S) to the analogous *anhydro*-5-mercapto-2,3,4-triphenyl-*s*-triazolium hydroxide (**6**, $R_1 = R_2 = R_3 = Ph$; X = S) occurred with such great ease that the intermediate benzoyl compound was not isolated on treatment of 1,4-diphenylthiosemicarbazide with benzoyl chloride. The formation of this *meso* ionic compound by the action of thiophosgene on N-amino-N,N′-diphenylbenzamidine was also an extremely facile reaction. These ready cyclizations were characteristic of the sul-

(1) (a) 1,2,4-Triazoles. XVII. (b) Support of this work by the U. S. Atomic Energy Commission, Contract AT-(40-1)-3016, is gratefully acknowledged. (c) Presented in part as a preliminary communication: K. T. Potts, S. K. Roy, and D. P. Jones, *J. Heterocyclic Chem.*, **2**, 105 (1965).

(2) K. T. Potts, H. R. Burton, T. H. Crawford, and S. W. Thomas, *J. Org. Chem.*, **31**, 3522 (1966), and earlier references listed therein.

(3) For recent reviews, see F. H. C. Stewart, *Chem. Rev.*, **64**, 129 (1964); Y. Noel, *Bull. Soc. Chim. France*, 173 (1964).

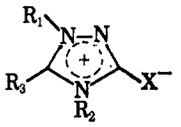
(4) (a) A. Schönberg, *J. Chem. Soc.*, 824 (1938); (b) F. L. Warren, *ibid.*, 1100 (1938).

(5) (a) M. Busch and co-workers, *Ber.*, **28**, 2635 (1895); (b) *ibid.*, **38**, 856, 4049 (1905); (c) *ibid.*, **43**, 3008 (1910); (d) *J. Prakt. Chem.*, **60**, 218, 228 (1899); (e) *ibid.*, **67**, 201, 216, 246, 257, 263 (1903); (f) *ibid.*, **74**, 501, 533 (1906).

(6) (a) W. Baker and W. D. Ollis, *Quart. Rev.* (London), **11**, 15 (1957); (b) see also G. F. Duffin, J. D. Kendall, and H. R. J. Waddington, *J. Chem. Soc.*, 3799 (1959).

TABLE I

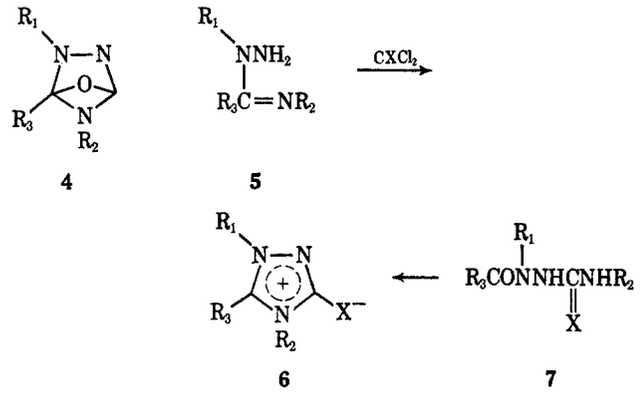
SOME *meso* IONIC COMPOUNDS OF THE *s*-TRIAZOLE SERIES



							Calcd, %			Found, %			Spectral data		
R_1	R_2	R_3	X	Mp, °C	Solvent	Formula	C	H	N	C	H	N	λ_{max}, mμ	Log ε	$\nu_{C=O}^{KBr}$, cm^{-1}
CH_3	Ph	Ph	S	277–278	Methanol	$C_{15}H_{12}N_2S$	67.4	4.9	15.7	67.5	5.1	15.5	306, 239	3.48, 4.19	
CH_3	CH_3	Ph	S	270–272	Methanol	$C_{10}H_{11}N_3S$	58.5	5.4	20.5	58.4	5.6	20.3	296, 243	3.44, 4.23	
CH_3	CH_3	Ph	O	299–301	Acetone	$C_{10}H_{11}N_3O$	63.5	5.9	22.2	63.7	6.0	22.0	270	3.71	1660
p-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	S	351–352 dec	Acetone–methanol	$C_{20}H_{12}N_6O_6S$	51.7	2.6	18.1	51.9	2.4	18.3	260	4.65	
p-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	H	S	286–288 dec	Acetone–methanol	$C_{14}H_9N_5O_4S$	49.0	2.6	20.4	49.1	2.6	20.6	265	4.17	

fur-containing *meso* ionic products.[7] With the 4-phenylthiosemicarbazide derivatives cyclization occurred with much greater ease than with the corresponding 4-methyl compounds and with the latter, the intermediate 1-acylthiosemicarbazides usually were isolated and cyclization was effected by heating above their melting points. The nature of the substituent attached to N-1 had little influence on the ease of cyclization. The corresponding semicarbazide derivatives often did not undergo cyclization to the *meso* ionic system under the influence of heat alone and deep-seated decomposition of the molecule sometimes occurred. Thus, 1-benzoyl-1-methyl-4-phenylsemicarbazide gave N,N′-diphenylurea, most likely formed by hydrolysis of phenyl isocyanate obtained by decomposition of the semicarbazide derivative. These are described in the Experimental Section.

By using either of the above general routes several additional *meso* ionic systems described in Table I have been prepared. The choice of the method used

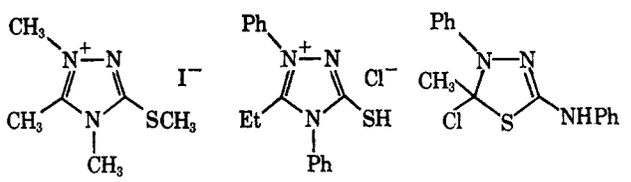


4 5 6 7

depends essentially on the ease of preparation of the starting products and, as will be shown in later communications, the general synthetic principle is capable of extension to the preparation of several other *meso* ionic systems. The appropriately substituted semicarbazides and thiosemicarbazides were readily prepared by reaction of the 1-acyl-1-substituted hydrazine with an isocyanate or thiocyanate, and the hydrazidines were usually readily available from an imino chloride and the appropriate hydrazine. Details of these preparations are described in the Experimental Section.

(7) This is illustrated by 1-benzoyl-1-methyl-4-phenylthiosemicarbazide which has previously been reported [R. L. Hinman and D. Fulton, *J. Am. Chem. Soc.*, **80**, 1895 (1958)] as melting with evolution of a gas and yielding a higher melting product which was not identified. This product is now regarded as *anhydro*-3,4-diphenyl-5-mercapto-2-methyl-*s*-triazolium hydroxide.

The sulfur-containing products are strong nucleophiles[5] and react readily with mineral acids or methyl iodide[6b] to form salts of the type described in Table II, in contrast to the oxygen-containing products. Thus, *anhydro*-5-mercapto-2,3,4-trimethyl-*s*-triazolium hydroxide reacted readily with methyl iodide to give the corresponding methiodide, 5-methylthio-2,3,4-trimethyl-*s*-triazolium iodide (**8**). The salt (**8**) reverted to the *meso* ionic product on treatment with pyridine or on heating. This ready conversion is indicative of the considerable resonance stabilization of the *meso* ionic system. Similarly, treatment of these sulfur-containing products with dry hydrogen chloride yielded

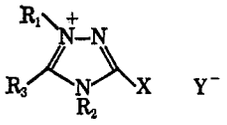


8 9 10

the corresponding salt such as 2,4-diphenyl-3-ethyl-5-mercapto-*s*-triazolium chloride (**9**) (ν_{SH} 2760 cm^{-1}). This same product was obtained directly from the action of propionyl chloride on 1,4-diphenylthiosemicarbazide. The conversion of these salts into the corresponding *meso* ionic systems with loss of hydrogen chloride also readily occurred on heating above their melting points or on heating with pyridine. In our studies the only exception was found in the case of (**9a**) which underwent rearrangement as described below. The improbable structure (**10**) had previously been assigned[8] to the product from acetyl chloride and 1,4-diphenylthiosemicarbazide and a reinterpretation of this work in terms of structure (**9a**) is now in order. At this stage of the investigation it became clear that the product obtained from the reaction of 1,4-diphenylthiosemicarbazide and acetic anhydride was not the expected *anhydro*-2,4-diphenyl-5-mercapto-3-methyl-*s*-triazolium hydroxide (**6**, $R_1 = R_2 = Ph$; $R_3 = CH_3$; X = S) but rather an isomeric product, 1,4-diphenyl-3-methyl-*s*-triazoline-5-thione (**11**). This structure was assigned to this product on the basis of analytical and

(8) (a) J. L. McKee, *J. Chem. Soc.*, **107**, 1133 (1915); M. Busch and W. Renner, *Ber.*, **67B**, 384 (1934). (b) The formation of 1-acetyl-2-phenylhydrazine can be envisaged as occurring through the intermediacy of **14** involving attack of N-2 on the S-acetyl group or by rearrangement of 1-acetyl-1-phenylhydrazine. Rearrangements of the latter type have been described: T. Taguchi, J. Ishibashi, T. Matsuo, and M. Kojima, *J. Org. Chem.*, **29**, 1097 (1964); C. Ainsworth, *Can. J. Chem.*, **43**, 1607 (1965).

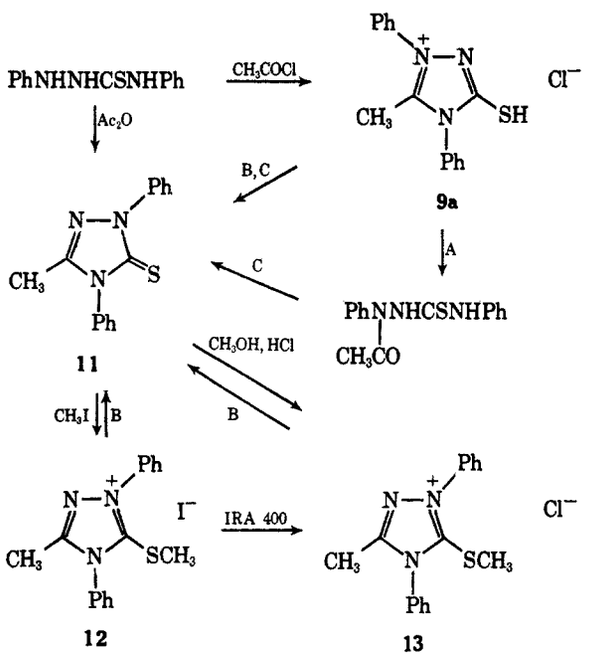
TABLE II
SOME SUBSTITUTED s-TRIAZOLIUM SALTS[a]



							Calcd, %			Found, %			Ultraviolet absorption data λ_{max}, mμ	Log ε
R_1	R_2	R_3	X	Y	Mp, °C	Formula	C	H	N	C	H	N		
Ph	Ph	CH_3	SH	Cl	232–234	$C_{15}H_{14}ClN_3S$	59.3	4.65	13.85	59.4	4.45	13.8	255	4.19
													314	3.73
Ph	Ph	Et	SH	Cl	230	$C_{16}H_{16}ClN_3S$	60.5	5.1	13.2	62.5	5.2	13.8	251	4.20
													311	3.53
Ph	CH_3	CH_3	SH	Cl	245 dec	$C_{10}H_{12}ClN_3S$	49.7	5.0	17.4	49.6	5.1	17.2	245	3.83
													301	3.59
Ph	CH_3	Et	SH	Cl	258–260 dec	$C_{11}H_{14}ClN_3S$	51.7	5.5	16.4	51.6	5.7	16.5	301	3.60
													Strong end absorption	
Ph	Ph	Ph	NH_2	Br	302	$C_{20}H_{17}BrN_4$	61.1	4.4	14.2	60.8	4.5	14.1	272	4.96
CH_3	Ph	Ph	NH_2	Br	228–229	$C_{15}H_{15}BrN_4$	54.4	4.5	16.9	54.6	4.7	16.6	265	4.54
Ph	Ph	H	SCH_3	I	236–238 dec	$C_{15}H_{14}IN_3S$	45.6	3.5	10.6	45.6	3.6	10.5	220	4.50
													265	4.87
CH_3	CH_3	CH_3	SCH_3	I	162–163	$C_6H_{12}IN_3S$	25.3	4.2	14.7	25.6	4.5	14.6	220	4.30

[a] All formed colorless needles from methanol or methanol–ether.

SCHEME I

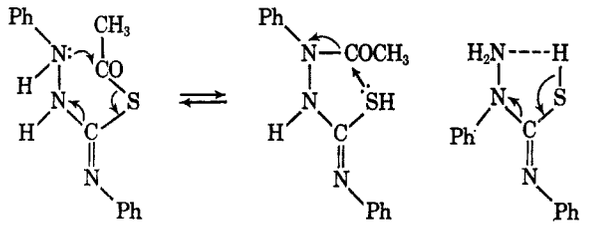


A = warm water, B = pyridine at reflux, C = heat above melting point

spectral data and from its behavior in the series of transformations shown in Scheme I.

Reaction of 1,4-diphenylthiosemicarbazide with acetyl chloride, either at room temperature or at reflux, gave an excellent yield of the salt (**9a**) previously described as an addition product of the two reactants, and the properties of **9a** were consistent with those described earlier.[8] Treatment of **9a** with warm water gave 1-acetyl-1,4-diphenylthiosemicarbazide (ν_{CO} 1626 cm^{-1}) also prepared from 1-acetyl-1-phenylhydrazine and phenyl isothiocyanate.[8] When the acyl compound was heated above its melting point, it readily lost 1 mole of water giving 1,4-diphenyl-3-methyl-s-triazoline-5-thione (**11**). This same product was obtained from 1,4-diphenylthiosemicarbazide and hot acetic anhydride and also directly from the salt (**9a**) on heating in pyridine or heating above its melting point. The 5-thione (**11**) reacted sluggishly with methyl iodide to form 1,4-diphenyl-3-methyl-5-methylthio-s-triazolium iodide (**12**) that reverted back, also sluggishly, to the thione on heating with pyridine or aniline. The iodide was converted into the corresponding chloride (**13**) which was also formed from the thione and methanolic hydrogen chloride. The latter reaction was reversed on heating with pyridine. Particularly noteworthy in these reactions is the longer reaction periods required when compared to corresponding reactions involving the exocyclic, sulfur-containing *meso* ionic products. The ultraviolet absorption spectrum of the salt (**9a**) is consistent with those of other salts of this type (Table II) whereas that of the salt (**13**) has strong end absorption only indicating a different chromophoric system.

The formation of **11** requires either a phenyl migration to occur in the *meso* ionic product or a dissociation–recombination process to be involved at some stage of the process. Only 1,4-diphenylthiosemicarbazide gave a rearranged product such as **11**; 4-methyl-1-phenylthiosemicarbazide and acetic anhydride formed the *meso* ionic product, *anhydro*-3,4-dimethyl-5-mercapto-2-phenyl-s-triazolium hydroxide (**6**, R_1 = Ph; R_2 = R_3 = CH_3; X = S), in the normal way. That dissociation–recombination of the thiosemicarbazide occurred, followed by ring closure to **11**, is supported by the isolation of a small amount of 1-acetyl-2,4-diphenylthiosemicarbazide from the reaction of acetic anhydride on 1,4-diphenylthiosemicarbazide.[8a] This was also obtained from 2,4-diphenylthiosemicarbazide and acetic anhydride. The hydrogen atom attached to N-4 of 1,4-diphenylthiosemicarbazide would be expected to be the most acidic one and it is plausible that, initially, the S-acetyl compound (**14**) is formed which can then dissociate to form either 1-acetyl-1-phenylhydrazine or 1-acetyl-2-phenylhydrazine and phenyl isothiocyanate.[8b] Formation of 1-acetyl-2,4-



14 15 16

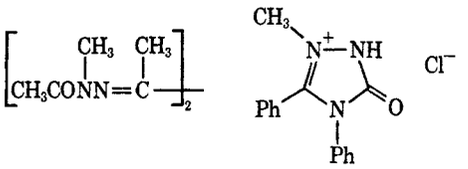
diphenylthiosemicarbazide with subsequent cyclization to the thione (**11**) could then occur. The hypothetical intermediate (**14**) is also helpful for explaining the thermal conversion of 1-acetyl-1,4-diphenylthiosemicarbazide to the thione (**11**). It is possible for an equilibrium to exist between **14** and **15** and this would be shifted in the direction of **14** owing to its dissociation to 1-acetyl-2-phenylhydrazine and phenyl isothiocyanate. Similar reasoning can be used to explain two further pieces of experimental evidence. The salt (**9a**) readily gives the thione (**11**) on heating above its melting point or on refluxing in pyridine, and when warmed gently with excess alcoholic potassium hydroxide solution, 1-acetyl-2,4-diphenylthiosemicarbazide is formed.[8] It is important to note that a major influence on this rearrangement is the acidity of the proton at position 4 due to the phenyl group and the ease with which these cyclic thiosemicarbazides undergo rearrangement. A related reaction of interest is the ready rearrangement of 2,4-diphenylthiosemicarbazide to 1,4-diphenylthiosemicarbazide on heating above its melting point or in the presence of a small amount of acid.[9] The infrared spectrum of 2,4-diphenylthiosemicarbazide indicated strong hydrogen bonding to be present and it is most likely that a cyclic mechanism is involved. By the electron transitions shown in **16**, a dissociation–recombination process can account for this rearrangement in a manner analogous to those above. Once again the 4-phenyl group is essential for the rearrangement to occur. Also it was found that 2,4-diphenyl-S-methylthiosemicarbazide was quite stable and did not undergo rearrangement under analogous conditions.

The pmr spectra of these *meso* ionic compounds were consistent with the assigned structures. The chemical shifts of the 3 protons (in DMSO) occurred at very low field; thus, in *anhydro*-2,4-diphenyl-5-mercapto-*s*-triazolium hydroxide the chemical shift was τ 1.02 and the phenyl protons absorbed in the range 1.97–2.39. Replacement of the exocyclic sulfur atom with an oxygen atom resulted in a low-field shift of the 3 proton to τ −0.1 (phenyl protons, τ 2.09–2.46) and this 3 proton also absorbed at −0.2 in nitron (**2**).

The above *meso* ionic systems did not take part in 1,3-dipolar addition type reactions with ethyl acetylenedicarboxylate, phenylacetylene, and tetracyanoethylene nor was it possible to effect bromination of the nucleus under conditions effective for sydnones. Nitration of *anhydro*-5-mercapto-2,3,4-triphenyl-*s*-triazolium hydroxide gave a trinitro product, *anhydro*-5-mercapto-2,3,4-tri(*p*-nitrophenyl)-*s*-triazolium hydroxide, identical with the product formed from *p*-nitrobenzoyl chloride and 1,4-di(*p*-nitrophenyl)thiosemicarbazide. Similarly, nitration of *anhydro*-2,4-diphenyl-5-mercapto-*s*-triazolium hydroxide gave a product where substitution had occurred in the phenyl groups.

The amino-substituted *s*-triazolium salts described in Table II were prepared very readily by reaction of the appropriate hydrazidine with cyanogen bromide. These salts, analogous to the sydnone imines, decomposed on attempted conversion into the corresponding bases.

During the preparation of 1-acetyl-1-methyl hydrazine[10] it became clear that an early report[11] describing this product as a crystalline solid, mp 98°, was incorrect. The data described in the Experimental Section show that this product was biacetyl (1-acetyl-1-methyl)-osazone (**17**).



17 18

The reaction of N-amino-N-methyl-N′-phenylbenzamidine (**5**, R_1 = CH_3; R_2 = R_3 = Ph) with phosgene is of particular interest. In contrast to the ready formation of the *meso* ionic compound with thiophosgene, the product obtained from the reaction with phosgene was found to contain ionic chlorine and, on heating above its melting point, readily gave 3,4-diphenyl-*s*-triazol-5-one.[12] These data indicate that this product is best represented as 3,4-diphenyl-2-methyl-*s*-triazol-5-onium chloride (**18**) and further illustrate the weak, nucleophilic character of the exocyclic oxygen atom in these products.

Experimental Section[13]

N-Amino-N,N′-diphenylbenzamidine and N-Phenylbenzamide Phenylhydrazone.—This procedure is a modification of that of Pechmann[14] and strict adherence to the following conditions results in reproducible yields. N-Phenylbenzimidoyl chloride[15] (57.0 g, 0.27 mole) in dry petroleum ether (350 ml, bp 30–60°) was treated dropwise, with stirring and with ice-bath cooling, with phenylhydrazine (63.0 g, 0.55 mole). After 4 hr the separated material was filtered, dried, and then extracted with dilute acetic acid (500 ml of 2%). Addition of ammonium hydroxide solution to the acetic acid extract (alkaline to litmus) precipitated N-amino-N,N′-diphenylbenzamidine as yellow prisms (16.0 g, 20%) mp 115°. It formed pale yellow plates from methanol: mp 116° (lit.[14] mp 119°); infrared, ($CHCl_3$) main bands 2874, 1600, 1575, 1481, 1337, 1145, 1070, 1020 cm^{-1}.

N-Amino-N,N′-diphenylbenzamidine was characterized as its benzal derivative which formed yellow prisms from methanol, mp 162° (lit.[14b] mp 159–160°).

The material, insoluble in the 2% acetic acid solution, crystallized from methanol and formed colorless needles (44.1 g, 56%) of N-phenylbenzamide phenylhydrazone: mp 175° (lit.[14] mp

(9) M. Busch and H. Holzmann, *Ber.*, **34**, 320 (1901).

(10) R. N. Hinman and D. Fulton, *J. Am. Chem. Soc.*, **80**, 1895 (1958).

(11) O. Diels and A. v. Drop, *Ber.*, **36**, 3183 (1903).

(12) M. Busch and J. Schneider, *J. Prakt. Chem.*, [2] **89**, 321 (1914).

(13) All melting points were taken in capillaries using an electrically heated block. Evaporations were done under reduced pressure on the steam bath using a Rotavap apparatus. Infrared spectra were determined on a Perkin-Elmer Model 421 spectrophotometer or a Baird IR2 spectrophotometer and ultraviolet spectra were obtained using a Beckman DK-2 spectrophotometer. Nmr spectra were measured on a Varian V-4302 dual-purpose, 60-Mc spectrometer using tetramethylsilane as internal standard and usual methods of calibration.

(14) (a) H. v. Pechmann, *Ber.*, **28**, 2366 (1895); (b) M. Busch and R. Ruppenthal, *ibid.*, **43**, 3001 (1910).

(15) O. Wallach and M. Hoffman, *Ann.*, **184**, 86 (1877); E. Hölljes and E. Wagner, *J. Org. Chem.*, **9**, 43 (1944).

174–175°); infrared ($CHCl_3$) main bands 3226, 2899, 1600, 1493, 1429, 1408, 1299, 1235, 1149, 1070, 1020 cm^{-1}.

A third product of the reaction, N,N′-diphenylbenzamidine was isolated by treating the alcoholic mother liquors from the recrystallization of N-amino-N,N′-diphenylbenzamidine with water. The precipitated material (1.2 g, 5%) crystallized from methanol as colorless needles, mp 144° alone or on admixture with a sample prepared from N-phenylbenzimidoyl chloride and aniline by the above method: infrared ($CHCl_3$) main bands 3226, 2857, 1613, 1575, 1493, 1478, 1429, 1342, 1316, 1093, 1064, 1022 cm^{-1}.

Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.8; H, 5.9; N, 10.3. Found: C, 83.9; H, 5.9; N, 9.8.

N-Amino-N-methyl-N′-phenylbenzamidine.—A solution of N-phenylbenzimidoyl chloride (21.5 g) in dry ether (100 ml) was slowly added to an ether solution of methyl hydrazine (9.2 g) at 0°. The solution was then stirred at room temperature for 1 hr. The ether solution was filtered from the solid and concentrated to an oily residue. The oil was treated with 50% aqueous acetic acid (200 ml) and extracted with ether. The aqueous solution was basified with ammonium hydroxide and extracted with ether. The ether solution was washed with water, dried ($MgSO_4$), and concentrated to a yellow oil (12.0 g), bp 125–128° (0.4 mm). The *p*-nitrobenzylidine derivative formed yellow plates from chloroform–methanol, mp 203–204° dec.

Anal. Calcd for $C_{21}H_{18}N_4O_2$: C, 70.4; H, 5.1; N, 15.6. Found: C, 70.3; H, 5.0; N, 15.6.

The hydrobromide crystallized from methanol–ether as colorless plates, mp 228–229° dec.

Anal. Calcd for $C_{14}H_{16}BrN_3$: N, 13.7. Found: 13.7.

1-Acetyl-4-methyl-1-phenylsemicarbazide.—A solution of 1-phenyl-4-methylsemicarbazide (25.0 g) in dry benzene (50 ml) was treated with acetyl chloride (22.4 g) and a brown, oily material soon separated. The reaction mixture was then heated to reflux for 90 min and, after cooling, the reddish brown solution gave a pasty product that was filtered and washed with benzene. The resultant, pinkish white solid (22.0 g, mp 136–142°) crystallized from methanol–ether as colorless, irregular prisms: mp 152–153°; infrared (KBr) main bands 3410, 3225, 3115, 2910, 1675, 1598, 1530, 1495, 1418, 1375, 1340, 1318, 1305, 1165, 1035, 1005, 900, 800, 755, 700 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}N_3O_2$: C, 58.0; H, 6.3; N, 20.3. Found: C, 58.1; H, 6.4; N, 20.3.

1-Benzoyl-4-methyl-1-phenylsemicarbazide.—A solution of 4-methyl-1-phenylsemicarbazide (17.1 g) in dry benzene was refluxed with benzoyl chloride (28.1 g) for 90 min. A white solid (16.0 g) separated and was recrystallized from acetic acid and finally from methanol from which it formed colorless needles: mp 235–236°; infrared (KBr) main bands 3390, 3250, 3130, 2930, 1660, 1640, 1595, 1545, 1493, 1450, 1372, 1312, 1095, 1080, 1030, 1005, 850, 820, 785, 758, 735, 705, 625 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.9; H, 5.6; N, 15.6. Found: C, 66.9; H, 5.7; N, 15.55.

The general procedures used for the preparation of 1-acyl-1,4-disubstituted semicarbazides and thiosemicarbazides from 1-acyl-1-substituted hydrazines and isocyanates and isothiocyanates are illustrated below.

1-Acetyl-1,4-dimethylsemicarbazide.—An ethereal solution of 1-acetyl-1-methyl hydrazine (8.0 g) on treatment with a solution of methyl isocyanate (8.0 g) in dry ether at room temperature gave a white solid (8.3 g, 63%) that crystallized from methanol as colorless platelets: mp 175–176°; infrared (Nujol) main bands 3175, 3077, 1667, 1626, 1538, 1307, 1250, 1145, 1031, 968 cm^{-1}.

Anal. Calcd for $C_5H_{11}N_3O_2$: C, 41.4; H, 7.6; N, 28.95. Found: C, 41.3; H, 7.7; N, 28.7.

1-Acetyl-1-methyl-4-phenylsemicarbazide was isolated as colorless needles (50%) from acetone–ether: mp 167–169°; infrared (KBr) main bands 3335, 3310, 3230, 1720, 1668, 1650, 1605, 1550, 1500, 1445, 1385, 1315, 1295, 1250, 1150, 1025, 760, 695 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}N_3O_2$: C, 57.95; H, 6.3; N, 20.3. Found: C, 57.8; H, 6.1; N, 20.2.

1-Benzoyl-1,4-dimethylsemicarbazide (85%) formed colorless needles from acetone–ether: mp 153–154°; infrared (KBr) main bands 3360, 3250, 2920, 1670, 1630, 1600, 1545, 1450, 1421, 1388, 1318, 1078, 800, 740, 700 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}N_3O_2$: C, 58.0; H, 6.3; N, 20.3. Found: C, 58.0; H, 6.3; N, 20.2.

1-Benzoyl-1-methyl-4-phenylsemicarbazide separated initially as an oil and then crystallized from acetone–ether forming colorless needles (70%): mp 171–172°; infrared (KBr) main bands 3330, 3245, 2915, 1700, 1664, 1638, 1600, 1554, 1502, 1445, 1375, 1319, 1296, 1245, 1090, 1075, 760, 724, 698 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.9; H, 5.6; N, 15.5. Found: C, 67.1; H, 5.7; N, 15.8.

1-Acetyl-1-methyl-4-phenylthiosemicarbazide (63%) crystallized from methanol or methanol–chloroform as colorless needles: mp 179–180° dec; infrared (KBr) main bands 3230, 3130, 3065, 2970, 1670, 1600, 1545, 1500, 1450, 1385, 1275, 1205, 1143, 1020, 750, 690 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}N_3OS$: C, 53.8; H, 5.8; N, 18.8. Found: C, 54.0; H, 5.9; N, 18.5.

1-Benzoyl-1,4-dimethylthiosemicarbazide crystallized from acetone–ether (42%) as colorless needles: mp 161–162°; infrared (KBr) main bands 3280, 3250, 3030, 2940, 1632, 1555, 1515, 1370, 1280, 1042, 726, 702, 663 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}N_3OS$: C, 53.8; H, 5.8; N, 18.8. Found: C, 53.5; H, 6.0; N, 18.6.

1-Benzoyl-1-methyl-4-phenylthiosemicarbazide (66%) separated from methanol as colorless needles, mp 153–155° dec, and was always contaminated with a small amount of the cyclized product formed during the recrystallization process. Short heating above its melting point converted it into the *meso* ionic product.

1,4-Di(*p*-nitrophenyl)thiosemicarbazide.—*p*-Nitrophenylisothiocyanate[16] (7.2 g) was added to a solution of *p*-nitrophenylhydrazine (6.0 g) in an ethanol (60 ml)–acetic acid (20 ml) mixture at 70°. After 15 min at 70°, the reaction mixture was cooled and a deep brown product (8.0 g, 60%, mp 202° dec) separated. After digestion with ethanolic hydrochloric acid (60 ml of ethanol and 20 ml of concentrated acid) at 70° for 10 min, the residue (7.0 g, mp 200–202° dec) was recrystallized from acetone–methanol (charcoal) whence it separated as yellow prisms, mp 207–209° dec.

Anal. Calcd for $C_{13}H_{11}N_5O_4S$: C, 46.85; H, 3.3; N, 21.0. Found: C, 47.1; H, 3.5; N, 20.8.

The following procedures illustrate the methods used for the preparation of the *meso* ionic compounds.

***anhydro*-5-Hydroxy-2,3,4-triphenyl-*s*-triazolium Hydroxide. A. Phosgene Method.**—N-Amino-N,N′-diphenylbenzamidine (5.0 g) dissolved in dry benzene (50 ml) was heated on a steam bath while phosgene was bubbled into the solution. On concentration and cooling of the reaction mixture, white needles separated (5.2 g, 96%): mp 316° (lit.[5] mp 301–302°) (the melting point was not raised on crystallization from methanol); infrared (KBr) main bands 3060, 2930, 1675, 1595, 1505, 1470, 1450, 1350, 1320, 1200, 1160, 1096, 1070, 1030, 1005, 915, 782, 775, 748, 710, 700, 670 cm^{-1}.

Anal. Calcd for $C_{20}H_{15}N_3O$: C, 76.7; H, 4.8; N, 13.4. Found: C, 76.6; H, 4.9; N, 13.4.

B. By Cyclization of 1-Benzoyl-1,4-diphenylsemicarbazide.—1,4-Diphenylsemicarbazide (5.0 g) was heated with benzoyl chloride (3.0 ml) on the steam bath. The precipitated benzoyl compound crystallized from methanol as white needles: 5.0 g (87%); mp 215°; infrared (KBr) main bands 3370, 3240, 3120, 3050, 1672, 1640, 1600, 1535, 1492, 1448, 1364, 1334, 1321, 1240, 1079, 848, 750, 725, 695, 625 cm^{-1}.

Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.5; H, 5.2; N, 12.7. Found: C, 72.5; H, 5.2; N, 12.9.

The benzoyl compound (1.0 g) was added to ethanol (20 ml) in which sodium (0.5 g) had previously been dissolved. On standing, white needles separated from the reaction mixture. The yield of the *meso* ionic product was 0.9 g (90%), mp 316°.

In an attempt to effect cyclization with an acetic anhydride–acetic acid mixture (50 ml of a 33% mixture), the benzoyl derivative (1.0 g) was heated under reflux for 12 hr. On evaporation of the solvent and crystallization of the residue from methanol, white needles, mp 113°, were obtained. These were identified as 1-benzoyl-2,2-diacetyl-1-phenyl hydrazine: infrared (KBr) main bands 3070, 2920, 1730, 1720, 1675, 1600, 1495, 1450, 1365, 1339, 1285, 1265, 1220, 990, 940, 780, 758, 725, 700, 665, 640, 590 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.9; H, 5.4; N, 9.5. Found: C, 69.0; H, 5.6; N, 9.3.

Confirmation of the structure of this diacetyl product was obtained by its synthesis from 2-acetyl-1-phenylhydrazine by benzoylation followed by acetylation using standard procedures.

(16) R. D. Coghill and T. B. Johnson, *J. Am. Chem. Soc.*, **47**, 184 (1925).

anhydro-**5-Mercapto-2,3,4-triphenyl-*s*-triazolium Hydroxide. A. Thiophosgene Method.**—N-Amino-N,N′-diphenylbenzamidine (14.4 g) was dissolved in chloroform (200 ml) to which thiophosgene (5.5 ml) was added dropwise. After a reflux period of 2 hr, the solvent was evaporated and the residue was recrystallized from methanol. It separated as yellow prisms (10.5 g, 64%) mp 325° (lit.[5] mp 319°).

B. By Cyclization of 1-Benzoyl-1,4-diphenylthiosemicarbazide.—1,4-Diphenylthiosemicarbazide (5.0 g) and benzoyl chloride (3 ml) were kept at room temperature for 1 hr. The material that separated was washed with methanol and recrystallized from acetic acid from which it separated as yellow prisms (5.7 g, 85%), mp 325°, alone or on admixture with the product from A above. The infrared spectra of these two products were identical.

anhydro-**3,4-Dimethyl-5-hydroxy-2-phenyl-*s*-triazolium Hydroxide.**—1-Acetyl-4-methyl-1-phenylsemicarbazide (1.0 g) was heated for 2 hr at 200–210° at which temperature, after melting, it resolidified. The yellow solid was dissolved in the minimum volume of methanol and diluted with ether, whence a yellowish solid (0.6 g) separated. Repeated crystallizations from methanol–ether gave colorless needles, mp 259–261° dec.

anhydro-**5-Mercapto-2,3,4-trimethyl-*s*-triazolium Hydroxide.**—A solution of 1-acetyl-1-methylhydrazine (8.0 g) in ether (60 ml) was treated with a solution of methyl isothiocyanate (10.0 g) in dry ether (20 ml) at room temperature. Colorless needles (9.0 g) of 1-acetyl-1,4-dimethylthiosemicarbazide, mp 175–177°, separated in 30 min: infrared (KBr) main bands 3290, 3140, 3000, 2930, 1670, 1575, 1513, 1385, 1272, 1140, 1072, 1015, 800, 773, 640 cm^{-1}. The acetyl product was heated at 220–230° for 30 min, and the *meso* ionic product was recrystallized from methanol whence it separated as colorless needles, mp 256–257° dec. On recrystallization from methanol, the acetyl product also underwent cyclization to the *meso* ionic compound.

Anal. Calcd: mol wt, 143. Found: mol wt, 143.

The *s*-triazolium salts described in Table II were prepared by one of the following general procedures.

4,5-Dimethyl-3-mercapto-1-phenyl-*s*-triazolium Chloride.—4-Methyl-1-phenylthiosemicarbazide (20.0 g) in dry benzene (50 ml) and acetyl chloride (15 ml) were heated together under reflux for 1.5 hr. An immediate exothermic reaction occurred with development of a pink coloration that gradually disappeared over the reaction period with hydrogen chloride being evolved. After approximately 20 min of reaction time, the contents of the flask solidified. This product was collected, washed with cold benzene, and dried, yielding 9.6 g of fine needles, mp 235° dec. The salt crystallized from methanol–ether as long, colorless needles, mp 241–242°. The salt (0.5 g) was refluxed in pyridine (3 ml) for 3 hr. Pyridine was removed under reduced pressure, the residue was treated with methanol, and the colorless precipitate (0.2 g) was recrystallized from acetonitrile–acetone. It separated as colorless plates, mp 288–290° dec, and was identical with *anhydro*-3,4-dimethyl-5-mercapto-2-phenyl-*s*-triazolium hydroxide (**6**, R_1 = Ph; R_2 = R_3 = CH_3; X = S).

3-Amino-1,4,5-triphenyl-*s*-triazolium Bromide.—N-Amino-N,N′-diphenylbenzamidine (2.9 g) and cyanogen bromide (1.1 g) in methanol (40 ml) were heated under reflux for 5 hr. The solvent was removed under reduced pressure, leaving a brittle residue that crystallized on trituration with acetone. It crystallized from methanol–ether as rosettes of colorless needles: 2.4 g, mp 302°; infrared (KBr) main bands 3100, 3040, 1640, 1505, 1485, 1384, 765, 695 cm^{-1}.

An alternative procedure that is used with heat-sensitive starting material is illustrated by the preparation of 3-amino-4,5-diphenyl-1-methyl-*s*-triazolium bromide. N-Amino-N-methyl-N′-phenylbenzamidine (1.0 g) in ether (30 ml) was treated with cyanogen bromide (0.6 g) in ether (30 ml) and the mixture was left at room temperature for 20 min. The white product that separated crystallized from a methanol–acetone–ether mixture as colorless needles: mp 228–229°; infrared (Nujol) main bands 3077, 2924, 1608, 1550, 1481, 1309, 1235, 1096, 1064, 760, 688 cm^{-1}.

5-Methylthio-2,3,4-trimethyl-*s*-triazolium Iodide.—*anhydro*-5-Mercapto-2,3,4-trimethyl-*s*-triazolium hydroxide (0.5 g) in methanol (20 ml) was treated with methyl iodide (2 ml) and the solution was left at room temperature for 30 min and then warmed gently for 15 min. Dilution of the methanol solution with ether gave a solid (0.4 g) which crystallized from methanol–ether as cream-colored needles: mp 162–163°; infrared (Nujol) main bands 1563, 1527, 1283, 971, 800, 732 cm^{-1}.

Basic Hydrolysis of *anhydro*-5-Hydroxy-2,3,4-triphenyl-*s*-triazolium Hydroxide.—The *meso* ionic compound (0.08 g), dissolved in hot methanol (15 ml), was heated under reflux with sodium hydroxide solution (15 ml of 10%) for 15 min. After cooling, the product that separated was collected and recrystallized from methanol, yielding 0.03 g (41%) of 1,4-diphenylsemicarbazide, mp 178° (lit.[17] mp 176°). Continuous ether extraction of the acidified filtrate yielded benzoic acid. The *meso* ionic compound was stable in boiling 10% sodium bicarbonate solution and in hot water.

Attempted Cyclization of 1-Benzoyl-1-methyl-4-phenylsemicarbazide. A.—The semicarbazide (1.0 g) was heated at 210–220° for 30 min and the melt, on trituration with aqueous methanol, solidified (0.32 g). It crystallized from methanol as colorless needles, mp 240–241° and was identified as N,N′-diphenylurea (lit.[18] mp *ca.* 235°) from infrared and mixture melting point data.

B.—The semicarbazide (2.0 g) in methanol (30 ml) was added to a solution of sodium methoxide (from 0.1 g of sodium) in methanol (20 ml) and then left at room temperature for 2 hr. The solution upon concentration and dilution with water, gave a solid (1.6 g) which crystallized from methanol as colorless, irregular prisms, mp 170°. The mixture melting point with the starting material was 170–171° and their infrared spectra were identical.

Cyclization of 1-Acetyl-1-methyl-4-phenylsemicarbazide. A.—The semicarbazide (3.0 g) was heated at 200–210° for 30 min. The melt afforded colorless needles, mp 220–232° (0.41 g), on crystallization from methanol. Further crystallization raised the melting point to 244–245°. This product was identified as N, N′-diphenylurea with which it had an identical infrared spectrum and showed no depression of the mixture melting point.

Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.35; H, 5.7; N, 13.2. Found: C, 73.4; H, 5.8; N, 12.8.

B.—The semicarbazide (2.0 g) in methanol (20 ml) was added to a solution of sodium methoxide (from 0.2 g of sodium) in methanol (20 ml) and then kept at room temperature for 2 hr. Dilution with water to 100 ml gave *anhydro*-2,3-dimethyl-5-hydroxy-4-phenyl-*s*-triazolium hydroxide (0.8 g) which crystallized from methanol as colorless needles: mp 204–205°; infrared (KBr) 3050, 2920, 1665, 1598, 1532, 1505, 1450, 1335, 1240, 1155, 905, 755, 695 cm^{-1}.

Anal. Calcd for $C_{10}H_{11}N_3O$: C, 63.5; H, 5.9; N, 22.2. Found: C, 63.2; H, 5.8; N, 21.9.

Attempted Cyclization of 1-Acetyl-1,4-dimethylsemicarbazide.—The semicarbazide (3.5 g) was heated at 230–234° for 1 hr. The hygroscopic melt was dissolved in methanol (5 ml) and treated with concentrated hydrochloric acid (15 drops) and then diluted with ether. The resultant solid (1.0 g) crystallized from methanol–ether and finally from methanol–acetone as colorless needles, mp 174–175°.

Anal. Found: C, 33.7; H, 6.5; N, 23.55.

Using lower fusion temperatures resulted in starting material being recovered, and no cyclization was obtained with sodium methoxide solution.

The Formation of 1,4-Diphenyl-3-methyl-*s*-triazolin-5-thione. A. Reaction of 1,4-Diphenylthiosemicarbazide with Acetic Anhydride.—1,4-Diphenylthiosemicarbazide (10.0 g) on heating on the steam bath for 2 hr with acetic anhydride (6 ml) gradually dissolved. After evaporation to dryness, the residue was washed with benzene and the oily residue, after trituration with methanol (15 ml), crystallized, mp 220–225°. After repeated crystallizations from methanol, 1,4-diphenyl-3-methyl-*s*-triazolin-5-thione was obtained as colorless rhombs: mp 236–237°, resolidifying and melting at 263–264°; infrared (KBr) main bands 3030, 2970, 1593, 1555, 1510, 1485, 1450, 1420, 1375, 1340, 1178, 1170, 1095, 995, 775, 745, 710, 695, 690, 660, 655 cm^{-1}.

Anal. Calcd for $C_{15}H_{13}N_3S$: C, 67.4; H, 4.9; N, 15.7. Found: C, 67.3; H, 4.7; N, 15.5.

B. Fusion of 1-Acetyl-1,4-diphenylthiosemicarbazide.—The acetyl compound (0.7 g), obtained as described below, was heated at 155–160° for 1 hr and slowly formed a dark liquid that solidified. The product, after repeated recrystallizations from methanol (charcoal), was obtained as small, colorless rhombs, mp 236–237°, resolidifying and melting at 262–264°. It was identical in all respects with the product from A above.

C. From 2,4-Diphenyl-5-mercapto-3-methyl-*s*-triazolium Chloride and Pyridine.—The chloro compound (1.0 g) was refluxed with pyridine (5 ml) for 2 hr. The pyridine was removed com-

(17) M. Busch and R. Frey, *Ber.*, **36**, 1369 (1903).
(18) A. Sonn, *ibid.*, **47**, 2440 (1914).

pletely under reduced pressure and the oily residue was washed with water and then induced to crystallize by the addition of methanol. It separated as colorless plates, mp 236–237°, resolidifying and melting at 260–262°. It was identical with the above products in all respects.

When the above chloride was heated at 225–230° for 10 min, a black, gummy residue was obtained. By the above work-up procedure the 5-thione was isolated.

2,4-Diphenyl-5-mercapto-3-methyl-s-triazolium Chloride.—1,4-Diphenylthiosemicarbazide (10.0 g) was suspended in dry benzene (10 ml) and acetyl chloride (6 ml) was added. After stirring for a short time, a yellow solution was formed that, after standing overnight, yielded a white product mixed with a little oily material. After dilution with more benzene, the white product was collected (6.3 g). It crystallized from methanol–ether (containing a few drops of concentrated hydrochloric acid) as colorless needles: mp 226–227° dec, with darkening at *ca.* 215°; infrared (KBr) main bands 3170, 3070, 2890, 2830, 2790, 1624, 1610, 1570, 1550, 1485, 1450, 1330, 1260, 1015, 838, 760, 742, 705, 690, 665 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}ClN_3S$: C, 59.3; H, 4.6; N, 13.8. Found: C, 59.5; H, 4.8; N, 13.9.

Similar results were obtained when the reaction was carried out at reflux temperature.

The corresponding picrate, prepared by the addition of a saturated solution of picric acid to a solution of the chloride in methanol, crystallized from methanol as yellow needles, mp 177–179°.

Anal. Calcd for $C_{21}H_{16}N_6O_7S$: C, 50.8; H, 3.55; N, 16.9. Found: C, 51.2; H, 3.0; N, 17.3.

1-Acetyl-1,4-diphenylthiosemicarbazide.—The above chloride (4.0 g) in water (100 ml) was slowly warmed on the steam bath for 1 hr. At this point the aqueous solution became turbid and a white, crystalline product separated (1.7 g, mp 168–169°). Purification for analysis was achieved by dissolving the product in cold methanol and then adding water, whence the acetyl product separated as colorless rhombs: mp 167–168°; infrared (Nujol) main bands 3030, 2941, 1645, 1572, 1504, 1290, 1263, 1183, 1124, 1064, 1022, 1005, 926 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}N_3OS$: C, 63.15; H, 5.3; N, 14.7. Found: C, 63.4; H, 5.3; N, 15.0.

Crystallization of this product from hot solvents resulted in cyclization to the 5-thione.

1,4-Diphenyl-3-methyl-5-methylthio-s-triazolium Iodide.[19]—The thione (0.5 g) in methanol (25 ml) was treated with methyl iodide (1 ml). After 12 hr at room temperature, the solution was concentrated, dry ether was added, and the white product that separated (0.6 g) was recrystallized from methanol–ether as colorless needles: mp 259–260° with sintering at 248°; infrared (Nujol) main bands 1575, 1548, 1504, 1285, 1256, 1031, 999, 966, 784, 760, 749, 713, 694, 682 cm^{-1}.

Anal. Calcd for $C_{16}H_{16}IN_3S$: C, 46.9; H, 3.9; N, 10.3. Found: C, 47.2; H, 4.2; N, 10.2.

The corresponding chloride was obtained by passing a solution of the iodide (0.5 g) in methanol through a column of IR-A 400 ion-exchange resin. It crystallized from methanol–ether as long, colorless needles: mp 240–242° dec; infrared (Nujol) main bands 1570, 1550, 1504, 1307, 1266, 1149, 1005, 789, 772, 746, 714, 699, 687 cm^{-1}.

Anal. Calcd for $C_{16}H_{16}ClN_3S$: C, 60.5; H, 5.0; N, 13.2. Found: C, 60.4; H, 5.2; N, 13.4.

The chloride was also obtained from a solution of the thione (0.3 g) in dry methanol (25 ml) that had been saturated with dry hydrogen chloride.

Treatment of 1,4-Diphenyl-3-methyl-5-methylthio-s-triazolium Salts with Pyridine.—The chloride (1.0 g) (or the iodide) was refluxed with pyridine (8 ml) for 15 hr. Pyridine was removed under reduced pressure and the residue washed with water. The semisolid residue crystallized from methanol as colorless rhombs, mp 236–237°, resolidifying and melting at 261–262°, and was identical with the 5-thione above.

When aniline was used as the base in this reaction, the reflux time required was reduced to 3 hr.

Hydrolysis of 1,4-Diphenyl-3-methyl-5-methylthio-s-triazolium Iodide.—The iodide (2.0 g) was refluxed with methanolic potassium hydroxide solution (100 ml of 5%) for 4 hr. Methanethiol was rapidly evolved and, after concentration of the reaction mixture, water (100 ml) was added and the reaction was extracted with ether (200 ml). After the usual work-up, a dark gummy residue was obtained. Trituration with ether gave a gray solid (0.54 g) that crystallized from methanol–ether (charcoal) as colorless needles, mp 175–176°. This was shown to be 1,4-diphenylsemicarbazide by direct comparison with an authentic specimen.

Nitration of *anhydro*-5-Mercapto-2,3,4-triphenyl-s-triazolium Hydroxide.—The above *meso* ionic compound (1.0 g) was added portionwise to concentrated sulfuric acid (15 ml) cooled in an ice bath. The resulting pink solution was treated dropwise with concentrated nitric acid (5 ml). The dark reaction mixture was then heated at 42° for 3 hr during which the color changed to green. The reaction mixture was poured into ice–water (150 ml) and the yellow product that separated was collected. After crystallization from acetone and finally from acetonitrile, *anhydro*-5-mercapto-2,3,4-tri(*p*-nitrophenyl)-*s*-triazolium hydroxide was obtained as yellow needles: mp 351–352° dec; infrared (Nujol) 1577, 1508, 1488, 1159, 1089, 974, 898, 870, 850, 812, 741, 738, 718, 692 cm^{-1}.

Anal. Calcd for $C_{20}H_{12}N_6O_6S$: C, 51.7; H, 2.6; N, 18.1. Found: C, 51.4; H, 2.6; N, 18.2.

Biacetyl (1-Acetyl-1-methyl)hydrazone.—Biacetyl acetylhydrazone[20] (65.0 g) in dimethylformamide (200 ml) was added in portions to a stirred and cooled suspension of sodium hydride (21.0 g, 53.5% oil suspension) in dimethylformamide (200 ml), when a copious evolution of hydrogen occurred.[21] After 30 min, the brown solution was treated with methyl iodide (42.0 ml) and stirred for 1 hr, and cold water (1200 ml) was added. The reaction mixture was saturated with sodium chloride and extracted with ether (1000 ml); the ether solution was washed with water (150 ml), dried ($CaCl_2$), and concentrated, when a greenish yellow oil was obtained. This was dissolved in petroleum ether (300 ml) and cooled to 0°, when a cream solid (32.0 g), mp 36–38°, separated. The mother liquor upon concentration and cooling gave another crop (10.0 g) of solid, mp 37–40°. The combined solid upon further crystallization from petroleum ether gave colorless needles, mp 42° (lit.[11] mp 43°).

1-Acetyl-1-methylhydrazine and Biacetyl (1-Acetyl-1-methyl)-osazone.—The above hydrazone (40.0 g) was dissolved in water (1500 ml) and heated to reflux and then distilled until the distillate no longer gave the odor of biacetyl. The aqueous solution was concentrated and the dark brown residue dissolved in chloroform. The chloroform solution was dried (Na_2SO_4) and concentrated. The oily residue was chromatographed on alumina (Woelm, activity II, 30.0 g) and eluted with chloroform (200 ml). Concentration of the chloroform solution gave an oil which distilled *in vacuo* and 1-acetyl-1-methylhydrazine was obtained as a pale yellow oil (9.0 g), bp 56° (0.6 mm) [lit.[10] bp 118–120° (24 mm)]. The *p*-nitrobenzylidene derivative separated as long, yellow needles, mp 186–188° (lit.[10] mp 187–188°).

The thick, brown, oily material that did not distil was dissolved in ether (20 ml), cooled, and a tan solid (0.54 g) was obtained. Biacetyl (1-acetyl-1-methyl)osazone crystallized from ether as colorless needles: mp 94–96°; infrared (KBr) 1650, 1600, 1480, 1400, 1420, 1365, 1330, 1220, 1140, 1108, 1025, 995, 955, 790, 655 cm^{-1}; nmr ($CDCl_3$) τ 7.8 (6 H, doublet, CCH_3 and $COCH_3$), 6.72 (3 H, singlet, NCH_3); no absorption in the ultraviolet.

Anal. Calcd for $C_{10}H_{18}N_4O_2$: C, 53.1; H, 8.0; N, 24.8. Found: C, 53.45; H, 8.2; N, 24.8.

The osazone absorbed 2 moles of hydrogen with the spectral characteristics of the reduction product being as follows: infrared (film) 3120, 1637 (main peaks) cm^{-1}; nmr ($CDCl_3$) unresolved multiplet τ 8.9 (6 H, 2-CCH_3), singlet at 7.86 (6 H, 2-$COCH_3$), singlet 6.96 (6 H, 2-NCH_3), an unresolved multiplet centered at 6.75 (2 H, >CH) and a broad peak at 5.0–5.9 (2 H, 2-NH).

Reaction of N-Amino-N-methyl-N′-phenylbenzamidine with Phosgene.—The benzamidine (2.4 g) in chloroform (50 ml) at 0° was treated with a fine stream of phosgene for 1 hr and a small amount of colorless product separated. After 2.5 hr at reflux temperature, the reaction mixture was cooled and the product was collected (2.1 g). 3,4-Diphenyl-2-methyl-s-triazol-5-onium chloride crystallized from methanol–ether as colorless needles, mp 185°, with frothing, solidifying, and remelting at 220–225°.

(19) The available data do not rigorously exclude methylation occurring at N-2, forming 2,3-dimethyl-1,4-diphenyl-s-triazol-5-thionium iodide. The chemical shifts of the methyl protons (determined in DMSO) at τ 6.61 (CCH_3) and 7.26 (SCH_3 or NCH_3), when compared with the data obtained from other products in this study, support the assigned structures.

(20) O. Diels, *Ber.*, **35**, 347 (1902).

(21) This excellent method has been used for the alkylation of amides; see *e.g.*, M. E. Kuehne, *J. Am. Chem. Soc.*, **83**, 1492 (1961).

Anal. Calcd for $C_{15}H_{14}ClN_3O$: N, 14.6. Found: N, 14.4.

The above salt (0.8 g) was heated at 190–200° for 5 min when the original solid, after melting with effervescence, resolidified. 3,4-Diphenyl-*s*-triazolin-5-one crystallized from methanol as colorless needles: 0.3 g, mp 258–260° (lit.[12] mp 254–256°, 260°), $\lambda_{max}^{CH_3OH}$ 256 mμ (log ε 3.96).

Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.9; H, 4.7; N, 17.7. Found: C, 70.6; H, 4.7; N, 17.95.

Registry No.—$C_{15}H_{14}ClN_3S$, 2254-71-9; picrate of $C_{15}H_{14}ClN_3S$, 13136-10-2; $C_{16}H_{16}ClN_3S$, 13136-11-3; $C_{10}H_{12}ClN_3S$, 13136-12-4; $C_{11}H_{14}ClN_3S$, 13136-13-5; $C_{20}H_{17}BrN_4$, 13136-14-6; $C_{15}H_{15}BrN_4$, 13127-53-2; $C_{15}H_{14}INS$, 13136-15-7; $C_6H_{12}IN_3S$, 2254-72-0; N-amino-N,N′-diphenylbenzamidine, 13136-17-9; N-phenylbenzamide phenylhydrazone, 13136-18-0; N-amino-N-methyl-N′-phenylbenzamidine-*p*-nitrobenzylidene derivative, 13136-19-1; N-amino-N-methyl-N′-phenylbenzamidine hydrobromide, 13136-20-4; 1-acetyl-4-methyl-1-phenylsemicarbazide, 13136-21-5; 1-benzoyl-4-methyl-1-phenylsemicarbazide, 13136-22-6; 1-acetyl-1,4-dimethylsemicarbazide, 13136-23-7; 1-acetyl-1-methyl-4-phenylsemicarbazide, 5790-59-0; 1-benzyl-1,4-dimethylsemicarbazide, 13136-25-9; 1-benzyl-1-methyl-4-phenylsemicarbazide, 13136-26-0; 1-acetyl-1-methyl-4-phenylthiosemicarbazide, 13136-27-1; 1-benzoyl-1,4-dimethylthiosemicarbazide, 13136-28-2; 1-benzoyl-1-methyl-4-phenylthiosemicarbazide, 13136-29-3; 1,4-di(*p*-nitrophenyl)thiosemicarbazide, 13136-30-6; 1-benzoyl-2,2-diacetyl-1-phenylhydrazine, 13136-31-7; N-amino-N-methyl-N′-phenylbenzamidine, 13136-32-8; 1,4-diphenyl-3-methyl-*s*-triazoline-5-thione, 13136-33-9; 1-acetyl-1,4-diphenylthiosemicarbazide, 13136-34-0; 1,4-diphenyl-3-methyl-5-methylthio-*s*-triazolium iodide, 13136-35-1; 1,4-diphenyl-3-methyl-5-methylthio-*s*-triazolium chloride, 13136-36-2; biacetyl (1-acetyl-1-methyl)hydrazone, 13136-37-3; biacetyl (1-acetyl-1-methyl)osazone, 13136-38-4; 3,4-diphenyl-2-methyl-*s*-triazol-5-onium chloride, 13136-39-5; 3,4-diphenyl-*s*-triazolin-5-one, 2039-00-1; 1-acetyl-1,4-dimethylthiosemicarbazide, 13136-41-9.

Oxidation of Phenylhydrazones with Manganese Dioxide

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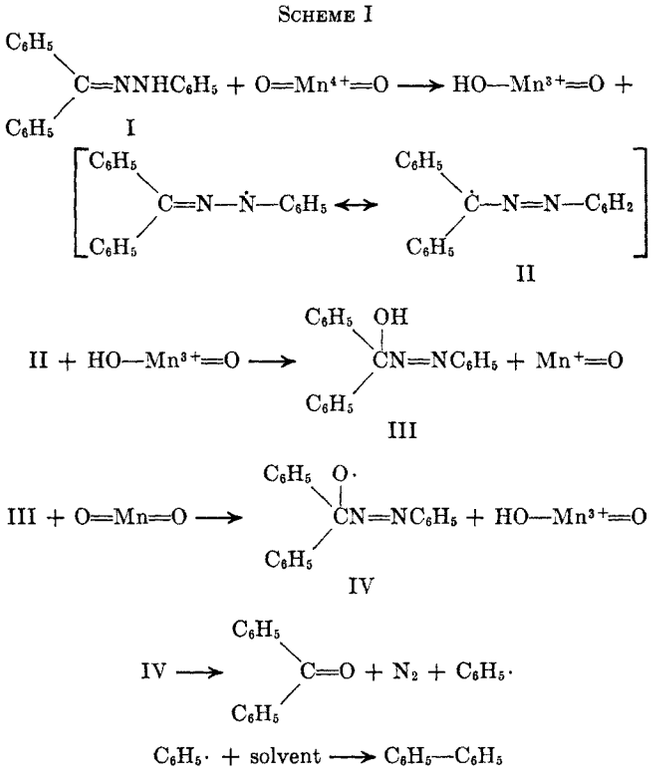
Benzophenone phenylhydrazone, acetophenone phenylhydrazone, and *p*-bromoacetophenone phenylhydrazone, when oxidized with manganese dioxide, give the corresponding ketones and biphenyl. Aldehyde phenylhydrazones, on the other hand, give a mixture of oxidative dimers, triazoles, and biphenyl, depending on the reaction conditions. Oxidation of benzil osazone gives 2,4,5-triphenyl-1,2,3-triazole, whereas biacetyl and glyoxal osazones give only azoalkanes.

Manganese dioxide has been employed in the oxidation of a variety of organic compounds.[2] Quite recently, the oxidation of several organic substrates like phenylcarbinols,[3] diarylmethanes,[4] N-methylanilines,[5] and of N-benzylanilines,[6] employing active manganese dioxide in neutral solvents, has been tried and a free-radical mechanism has been suggested for these reactions. Maier and Heep[7] have reported that hydrazones of aldehydes and ketones are oxidized by manganese dioxide to carbonyl compounds, and they have suggested that diazo ketones are the intermediates in these reactions.

During the course of the present investigation, we have examined the oxidation of several phenylhydrazones of aldehydes and ketones, employing manganese dioxide. Thus, the oxidation of benzophenone phenylhydrazone (I) in benzene at room temperature gave a mixture of benzophenone (50%) and biphenyl (27%).[8] When the same reaction, however, was carried out in refluxing benzene, higher yields of both benzophenone (65%) and biphenyl (34%) were obtained. The formation of biphenyl suggests that free-radical intermediates

SCHEME I



are involved in this reaction and a possible route is shown in Scheme I. In this scheme, we assume that manganese dioxide effects the cleavage of the N–H bond of the phenylhydrazone, generating the pseudo-

(1) To whom enquiries should be addressed.

(2) For a recent review, see, R. M. Evans, *Quart. Rev.* (London), **13**, 60 (1959).

(3) E. F. Pratt and J. F. Van de Castle, *J. Org. Chem.*, **26**, 2973 (1961).

(4) E. F. Pratt and S. P. Suskind, *ibid.*, **28**, 638 (1963).

(5) H. B. Henbest and A. Thomas, *J. Chem. Soc.*, 3032 (1957).

(6) E. F. Pratt and T. P. McGovern, *J. Org. Chem.*, **29**, 1540 (1964).

(7) G. Maier and U. Heep, *Angew. Chem. Intern. Ed. Engl.*, **4**, 956 (1965).

(8) The yields of biphenyl throughout are calculated on the basis that one phenyl radical from the hydrazone combines with the solvent in forming the product.