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Meso-ionic Compounds of the *s*-Triazole Series (I)

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Sir:

The concept of *meso*-ionic compounds advanced (2) to explain the structure of the sydnones has received further support by the synthesis (3) of similar products in related heterocyclic systems. We now wish to report studies on the synthesis and

characterization of a series of *meso*-ionic compounds containing the *s*-triazole nucleus which provide interesting evidence for the *meso*-ionic concept.

The suggestion for the representation as *meso*-ionic compounds of several bridged-ring systems prepared by Busch and co-workers (4) was originally

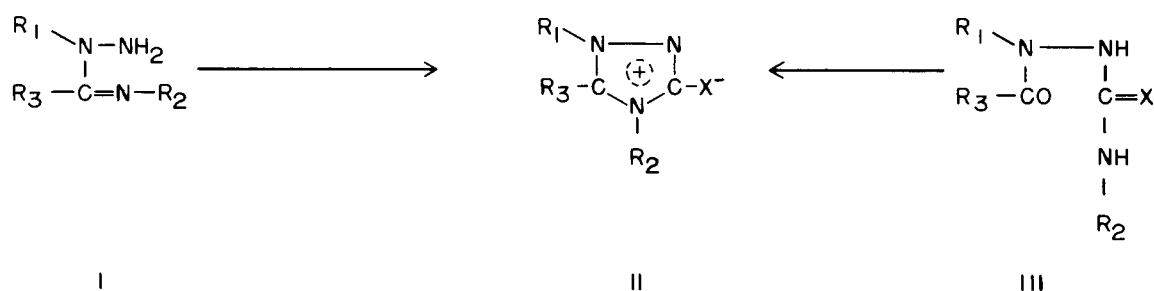
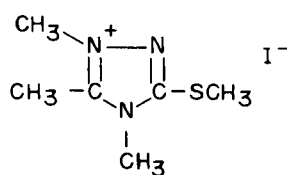


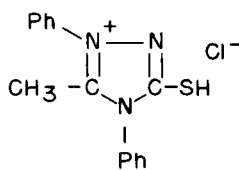
TABLE 1

Meso-ionic Compounds of the *s*-Triazole Series

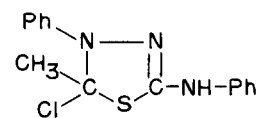
| R ₁ | R ₂ | R ₃ | X | M. p. °C | Ultraviolet Absorption Data | |
|-----------------|-----------------|-----------------|---|----------|-----------------------------|-------|
| | | | | | λ max mμ | log ε |
| Ph | Ph | Ph | O | 316 | 290 | 3.84 |
| Ph | Ph | Ph | S | 325 | 316 | 3.44 |
| | | | | | 241 | 4.34 |
| Ph | Ph | H | O | 260 | 292 | 4.01 |
| | | | | | 223 | 4.22 |
| Ph | Ph | H | S | 215-216 | 314 | 3.44 |
| | | | | | 245 | 4.31 |
| Ph | Ph | CH ₃ | S | 262 | 240 | 3.92 |
| Ph | CH ₃ | Ph | O | 238-239 | 286 | 3.82 |
| Ph | CH ₃ | CH ₃ | O | 259-261 | 262 | 3.80 |
| Ph | CH ₃ | CH ₃ | S | 294-295 | 242 | 4.15 |
| Ph | CH ₃ | H | O | 300-302 | 278 | 3.86 |
| Ph | CH ₃ | H | S | 262 | 302 | 3.40 |
| | | | | | 248 | 4.32 |
| CH ₃ | CH ₃ | CH ₃ | S | 256-257 | 242 | 4.15 |
| CH ₃ | Ph | CH ₃ | O | 244-245 | 239 | 4.31 |
| CH ₃ | Ph | CH ₃ | S | 244-246 | 240 | 3.92 |



IV



V



VI

made by Baker (2), though nitron was represented by polar structures nearly a decade earlier (5). In our work we have obtained confirmation of this suggestion and moreover have established these products as belonging to the *s*-triazole system and not the alternative, isomeric oxidiazole or thiadiazole ring systems. The correct skeletal arrangement of atoms was indicated by the synthesis of several of the products using ring closures at different portions of the molecule in such a way that skeletal rearrangements were precluded. The ring systems were also degraded to products that confirmed the assigned structures.

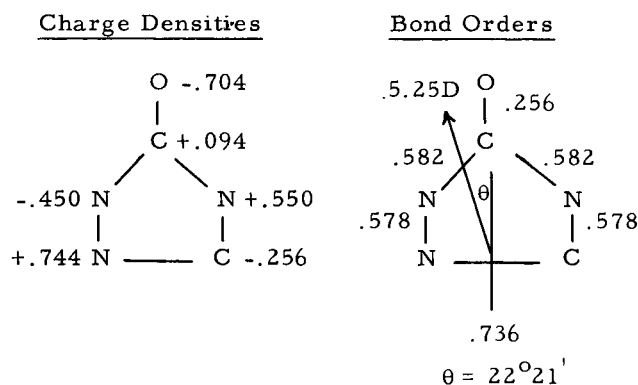
This approach is illustrated by the synthesis, among others, of anhydro-5-hydroxy-2,3,4-triphenyl-*s*-triazolium hydroxide (II; $R_1 = R_2 = R_3 = \text{Ph}$; $X = \text{O}$) by the action of phosgene on *N*-amino-*N,N'*-diphenylbenzamide (I; $R_1 = R_2 = R_3 = \text{Ph}$) and also by the ring closure of 1-benzoyl-1,4-diphenylsemicarbazide (III; $R_1 = R_2 = R_3 = \text{Ph}$; $X = \text{O}$) with sodium ethoxide. The latter cyclization could not be effected with acidic cyclodehydration agents or by heat, whereas the corresponding cyclization of 1-benzoyl-1,4-diphenylthiosemicarbazide to the analogous anhydro-5-mercapto-2,3,4-triphenyl-*s*-triazolium hydroxide (II; $R_1 = R_2 = R_3 = \text{Ph}$; $X = \text{S}$) occurred with such great ease that the intermediate benzoyl compound was not isolated on treatment of 1,4-diphenylthiosemicarbazide with benzoyl chloride. This *meso*-ionic compound was also obtained with great ease by the action of thiophosgene on *N*-amino-*N,N'*-diphenylbenzamide. The facile cyclizations were characteristic of the sulfur containing *meso*-ionic products (6). Anhydro-5-hydroxy-2,3,4-triphenyl-*s*-triazolium hydroxide was stable in the presence of hot, dilute mineral acid but with hot, 10% sodium hydroxide solution ring fission occurred yielding 1,4-diphenylthiosemicarbazide and benzoic acid. A similar behavior was observed with the corresponding sulfur containing *meso*-ionic system (II; $R_1 = R_2 = R_3 = \text{Ph}$; $X = \text{S}$) which was degraded to 1,4-diphenylthiosemicarbazide.

By using either of the above general routes the *meso*-ionic systems described in Table 1 have been prepared (7).

The assignment of *meso*-ionic type structures to these products was made on the basis of analytical data, molecular weight data (determined by mass spectrometry), and spectral data, especially the absence in the infrared region of -OH, -NH, and -SH absorptions, a distinctive feature of the spectra when compared to those of the starting products. In keeping with the increased ionic character of the carbonyl group, the carbonyl absorption in the oxygen containing *meso*-ionic systems shows an appreciable shift to lower frequency when compared to that of a carbonyl group in an *s*-triazolone. Thus, in anhydro-2,3,4-triphenyl-*s*-triazolium hydroxide the $\nu(\text{C}=\text{O})$ occurs at 1675 cm^{-1} and in 1,2,4-triphenyl-*s*-triazol-5-one the $\nu(\text{C}=\text{O})$ occurs at 1705 cm^{-1} . The ultraviolet absorption of the nucleus, as represented by anhydro-5-mercapto-2,3,4-trimethyl-*s*-triazolium hydroxide (II; $R_1 = R_2 = R_3 = \text{CH}_3$; $X = \text{S}$) had λ

max $242\text{ m}\mu$ ($\log \epsilon 4.15$) and the effect of various substituents on this absorption can be seen from Table 1.

In agreement with the proposed structures, anhydro-5-mercapto-2,3,4-trimethyl-*s*-triazolium hydroxide reacted readily with methyl iodide (as do all the other sulfur containing *meso*-ionic systems) to give the corresponding methiodide which is best represented as 5-methylthio-2,3,4-trimethyl-*s*-triazolium iodide (IV). The salt (IV) 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 hydrogen chloride yielded the corresponding salt such as 2,4-diphenyl-3-methyl-5-mercapto-*s*-triazolium chloride (V) ($\nu \text{SH} = 2790\text{ cm}^{-1}$). This same product was obtained directly from the action of boiling acetyl chloride on 1,4-diphenylthiosemicarbazide, and the conversion of these salts into the corresponding *meso*-ionic systems also readily occurred on heating with loss of hydrogen chloride. The improbable structure (VI) 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 (V) is now in order. Application of the Hückel LCAO Method (9) to the oxygen-containing *meso*-ionic system indicated that the system was a stable one with the charge densities and bond orders shown below. The theoretical dipole moment for the system was calculated to be approximately 5.25 D in the direction shown and this is of the same order as that found for the sydnone system. The predicted single bond character of the exocyclic carbon-oxygen bond is reflected in the low carbonyl absorption frequency of these oxygen-containing *meso*-ionic systems.



Acknowledgment.

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REFERENCES

- (1a) Part X in the series, 1,2,4-Triazoles; (b) National Science Foundation Undergraduate Research Participant, 1962-1963.
- (2) Reviews that summarize the evidence in this area are available: W. Baker and W. D. Ollis, *Quart. Rev.*, **11**, 15 (1957); F. H. C. Stewart, *Chem. Rev.*, **64**, 129 (1964); Y. Noel, *Bull. soc. chim. France*, 173 (1964).
- (3) Anhydro-2,4-diphenyl-3-methyl-5-hydroxyoxazolium hydroxide [R. Huisgen, H. Gotthardt, H. O. Bayer, and F. C. Schaefer, *Angew. Chem. Internat. Edit.*, **3**, 136 (1964)] and anhydro-2,3-diphenyl-5-hydroxy-1,3,4-oxadiazolium hydroxide [M. Hashimoto and M. Ohata, *Bull. Chem. Soc., Japan*, **34**, 668 (1961)] are two such examples.
- (4) Ref. 2 should be consulted for references relating to this early work; see also G. F. Duffin, J. D. Kendall and H. R. J. Waddington, *J. Chem. Soc.*, 3799 (1959).
- (5) F. L. Warren, *ibid.*, 1100 (1938); A. Schönberg, *ibid.*, 824 (1938).
- (6) 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.
- (7) All compounds prepared gave satisfactory analytical data.
- (8) M. Busch and W. Renner, *Ber.*, **67B**, 384 (1934); J. L. McKee, *J. Chem. Soc.*, 107, 1133 (1915).
- (9) Auxiliary inductive parameters were taken into account in these calculations.

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