MESOIONIC HETEROCYCLES AND HETEROCYCLIC BETAINE CATIONS (REVIEW)

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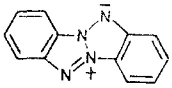
The first part of this review is devoted to correlation of the data of five foreign reviews and the original research and data of the author on the synthesis of mesoionic heterocycles that do not contain ionogenic substituents (heteroatoms) in the side chain. The compounds were classified as follows: mono-, bi-, and triheterocycles; sulfur-containing heterocycles; two-ring systems with one, two, or no nitrogen atoms in common and their condensed analogs. The preparation of betaine cations of methine dyes by three methods, viz., cyanine condensations of some quaternary salts and protonated azaindolizines and deprotonation of diquaternary salts of diheterylmethanes, is described in the second part of the review.

Mesoionic aromatic heterocycles, the first representative of which (I) has been known since 1962 [1] and was immediately included in a textbook [2], have still not been studied sufficiently, although they were the subject of reviews by Japanese chemists [3] in 1970 and American and West European researchers in 1977, 1978, and 1980 [4-7].



I

These compounds should be regarded as mesoionic heterocycles, in contrast, on the one hand, to mesoionic heterocyclic compounds and, on the other, to mesoionic forms of heterocycles that can also be represented in the normal neutral form. For example, it is assumed [8] that the properties of 1-substituted tetrazoles, particularly their UV spectra, reflect mesoionic structures better than neutral structures. As other examples of neutral heterocycles, the properties of which are determined in many respects by mesomeric mesoionic forms, one can cite pyrido- [9, 10] and pyrimido[1,2-b]indazoles [12], 1-methyl-α-carboline [11], some alkaloids [13], and many others. Mesoionic heterocyclic compounds, including such peculiar compounds as sydnones, contain ionogenic substituents (generally heteroatoms) in their side chains. Thus mesoionic heterocycles are those heterocycles whose mesoionic character is determined by the heterocyclic system itself without the participation of side substituents and are compounds that can be represented by means of structural formulas only by mesoionic structures.

Depending on the way in which they are fused, condensed aromatic nitrogen heterocycles can be divided into three groups, viz., those without a nitrogen atom in common, those with one nitrogen atom in common, and those with two nitrogen atoms in common. Prior to the discovery of mesoionic heterocycles, the last group of compounds was unknown; the first mesoionic heterocycles were representatives of precisely this class of condensed nitrogen heterocycles. The idea of mesoionic heterocycles proved to be quite novel and nontrivial and was not immediately asserted even among the discoverers, who initially assigned different nonmesoionic structures to the compounds obtained. This idea has made it possible and continues to make it possible to predict and synthesize new heterocyclic systems.

In the present review the above-mentioned reviews dealing with mesoionic heterocycles are revised and supplemented, and the application of the concepts of mesoionic heterocycles to a number of heterocyclic cations, which under certain conditions, particularly in the compositions of methine dyes, behave like mesoionic cations (betaine cations), is described.

T. G. Shevchenko Kiev State University, Kiev 252017. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 3-16, January, 1983. Original article submitted February 16, 1982.

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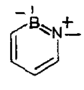
I. MESOIONIC HETEROCYCLES

1. MONOHETEROCYCLES AND THEIR CARBOCYCLIC DERIVATIVES

Mesoionic structures are not characteristic for normal monoheterocycles. Mesoionic boron—nitrogen heterocycles [14] such as systems II and III are classified as heteroorganic compounds and are not considered here. In the benzo-condensed five-membered heterocycle series the preparation of unstable indeno[2,1-d]thiazole IV has been reported (one of the mesomeric mesoionic structures is presented, although the negative charge may be placed on any carbon atom of the condensed carbo- or heterocycle, as well as in the ortho and para positions of the phenyl group). Compound IV, which can also be represented by a neutral structure with a tetravalent sulfur atom, is colored (λ_{max} in benzene = 550 nm) and displays negative solvatochromism [4, 15].



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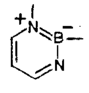

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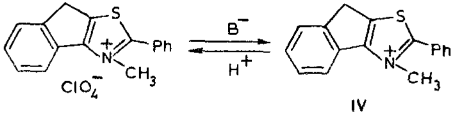
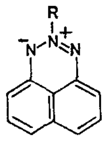


IV

Of the six-membered heterocycles, the most well known are 2-substituted naphtho[1,8-de]-1,2,3-triazines V and their derivatives [16-27]. Red and blue methyl-substituted derivatives were obtained by methylation of naphthotriazine at the beginning of this century [17], but the structure of the blue derivative (V, R = CH_3) was not established until 1964 [18].



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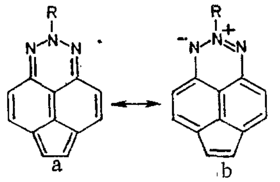

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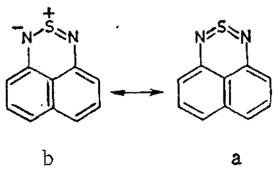
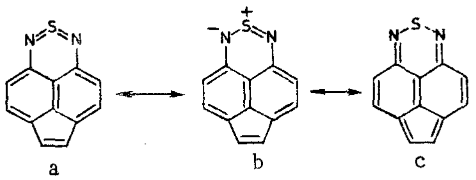
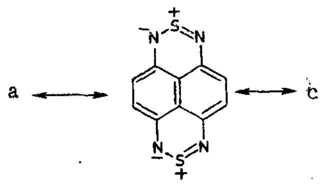


VII

In contrast to 1-substituted naphthotriazines, V react with radicals to give 4-, 6-, or 9-substituted products [20, 21]. Blue 2-amino derivatives V (R = NH_2) are formed along with red 1-amino derivatives from naphthotriazine by the action of chloramine [22]. Acenaphtho derivatives VI are more highly colored than their V analogs, and covalent structure VIa is possible for them [23, 25]. The same principle — heightening of the color on passing from the naphtho to the acenaphtho derivatives — is observed for sulfur analogs VII and VIII [26-28]. These compounds, like bisthiadiazine IX, which is also deeply colored [29], are not purely mesoionic compounds because of the existence of structures of the VIIIa and VIIIc type.*

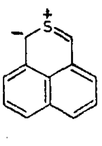


VIII

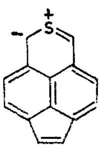


IX b

Mesoionic naphtho and acenaphtho derivatives of thiopyran X and XI are unstable; their adducts with dienophiles have been isolated [30, 31].



X



XI

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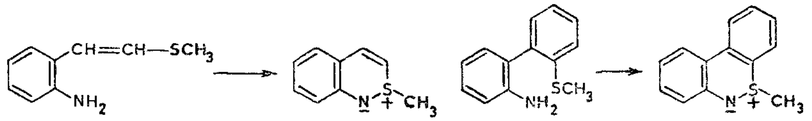
*According to the results of calculations and data from the photoelectronic spectra, a quinoid structure of the "c" type corresponds to IX and its Se analog [127].

Yellow XII and XIII, which are 2-azathiabenzene derivatives, were obtained by cyclization of the corresponding (methylthio)-substituted amines by means of N-chlorosuccinimide [32].


XII XIII

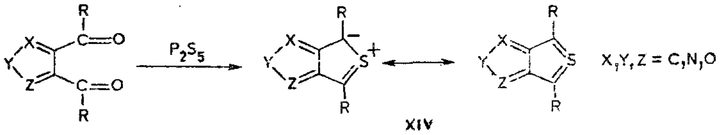
2. CONDENSED BIHETEROCYCLES

2.1 FIVE-MEMBERED HETEROCYCLES

2.1.1. [c]-Condensed Thiophenes and Other Five-Membered Sulfur Heterocycles

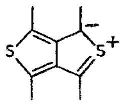
This group of heterocycles is given special treatment, since it includes both mesoionic heterocycles and compounds with tetravalent sulfur. Some quantum-chemical calculations show substantial participation of the d orbitals of sulfur in the formation of these structures, while others show just the opposite [5]. With respect to their chemical properties, there is every reason to regard these compounds, like the sulfur-containing compounds of section 1 and betaine cations (see below), as mesoionic heterocycles.

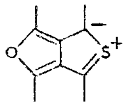
2.1.1.1. Without a Nitrogen Atom in Common. Condensed (at the c bond) thiophenes XIV, which are called "nonclassical condensed thiophenes," are obtained by annelation of the thiophene ring by means of phosphorus(V) sulfide.

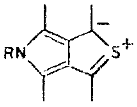


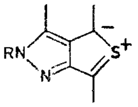
XIV

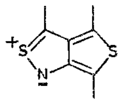
Of the nine possible [4] systems with the general formula XIV, eight (XV-XXII) are known (the thieno[3,4-c]isoxazole system is needed to complete the set). Not all XV-XXII have been isolated in individual form because of their instability, which depends on the nature of the heterocycle and the substituents. Thus the first stable thieno[3,4-c]thiophene was obtained in the form of a tetraphenyl derivative in 1969, but the corresponding diselenium analog could not be isolated in free form [33]. The unstable derivatives are "trapped" in the form of products of cycloaddition with electron-deficient dipolarophiles (acetylenedicarboxylic acid esters and other acetylenes, N-phenylmaleinimide, fumaronitrile, etc.). All of the compounds of this series are colored (λ_{max} 450-550 nm). Their characteristic reactions are the above-mentioned cycloaddition reactions with the formation of structures of the XXIII type, which is in agreement with the mesoionic nature of these systems [34-37]. Nonclassically condensed thiophenes were examined in greater detail in previous reviews [4, 38].


XV


XVI


XVII


XVIII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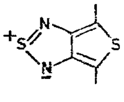
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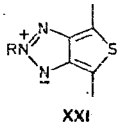
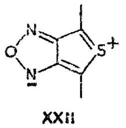
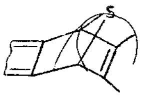
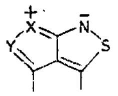

XXI

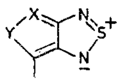

XXII


XXIII

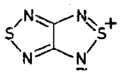
Of the 18 possible systems of the XXIV and XXV type, only systems XXVI and XXVII, which were obtained by the formation of a thiadiazole ring by the action of sulfur monochloride on the corresponding o-diamines [39, 40], are known. When selenious acid or its chloride was used in this reaction [40, 41], Se analogs XXVIII were obtained. The benzo analog of the XVIII system (XXIX) was synthesized by annelation of the thiophene ring, as shown above.



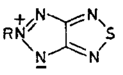
XXIV



XXV

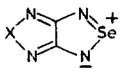


XXVI

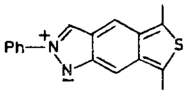


XXVII

XXVIII X = S, RN

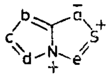


XXVIII



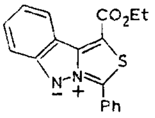
XXIX

2.1.1.2. With One Nitrogen Atom in Common. In contrast to the compounds of the preceding type, delocalization of the positive charge between the nitrogen and sulfur atoms is possible here, and the system is stabilized when yet another nitrogen atom that can accept negative charge is present in the system. In fact, of the many possible systems of this series (XXX), derivatives of thiazolo[3,4-b]indazole XXXI and condensed imidazoles XXXII-XXXV are known. Compound XXXI [43] is not a purely mesoionic heterocycle, since the negative charge can be placed in the side chain. Imidazoles XXXII and XXXIII were obtained by the general method for the synthesis of mesoionic condensed imidazoles with a nitrogen atom in common, viz., by condensation of nontautomeric α-amino azaheterocycles with α-halo ketones (a variant of the Chichibabin reaction) [44, 45]. This method has also been used to obtain other mesoionic imidazoles (see below).

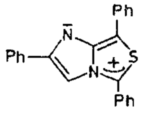


a, b, c, d, e = C, N

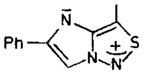
XXX



XXXI

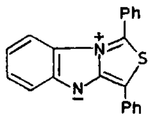


XXXII

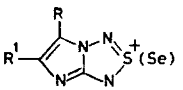


XXXIII

Thiazolobenzimidazole XXXIV is formed by the action of phosphorus pentasulfide on 1,2-dibenzoylbenzimidazole [46, 47], while imidazothia(selena)triazoles XXXV are formed by the action of sulfur chloride (selenium dioxide) on 1,2-diaminoimidazoles [48]; in contrast to XXXIV, XXXV are incapable of undergoing cycloaddition reactions.



XXXIV



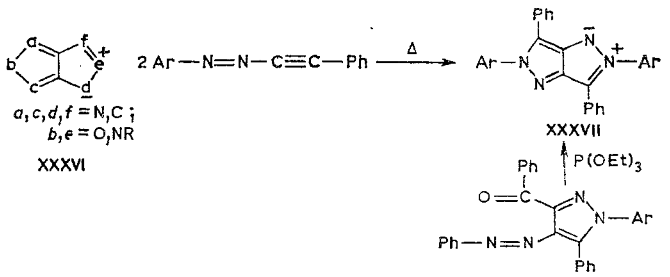
R = H, Ph ; R' = Ph; R-R' = C_6H_4

XXXV

2.1.2. Azapentalenes

It is known that the unstable 8π-electron pentalene system can be converted to stable aromatic 10π-electron systems by the introduction of nitrogen atoms into it; whereas only two types of compounds (those without nitrogen atoms in common and those with one nitrogen atom in common) are possible and are known in the series of "normal" nonmesoionic azapentalenes, a third type of compound (with two nitrogen atoms in common) is also known in the series of mesoionic azapentalenes.

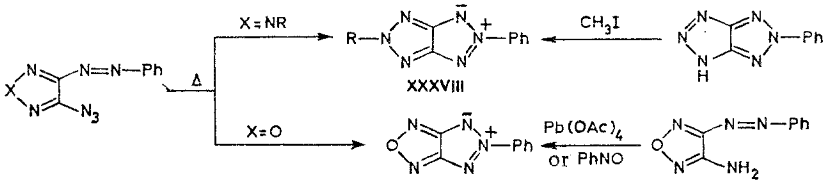
2.1.2.1. Without a Nitrogen Atom in Common. Of the 17 systems [4] of this type (XXXVI), the following three are known: pyrazolo[4,3-c]pyrazoles [49-52] (XXXVII), 1,2,3-triazolo[4,5-d]-1,2,3-triazoles [53] (XXXVIII), and 1,2,5-oxadiazolo[3,4-d]-1,2,3-triazoles [54, 55] (XXXIX), which were obtained as shown below.



$a,c,d,f = N,C$; $b,e = O,NR$

XXXVI

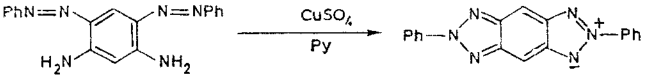
XXXVII



XXXVIII

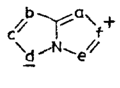
XXXIX

These compounds are quite stable; this is especially true for hexaazapentalene XXXVIII (R = Ph), in the catalytic hydrogenation of which cyclohexyl derivatives were obtained, i.e., the azapentalene system is more stable in this reaction than the benzene ring. It is assumed [5] that mesoionic benzobistriazole XL was obtained in 1921 via the scheme [56]



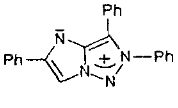
XL

2.1.2.2. With One Nitrogen Atom in Common. Only two systems (XLII and XLIII) of the 48 of the XLI general type have been obtained thus far: the first system was obtained by the above-mentioned variant of the Chichibabin reaction [44], while the second was obtained by cyclization of a substituted hydrazinotriazole [57]. The proton salts of XLII give mesoionic methine dyes (see section II), while salts of triazolo[3,4-c]triazole XLIII (both proton and quaternary salts) form normal methine dyes due to the activity of the methyl group.

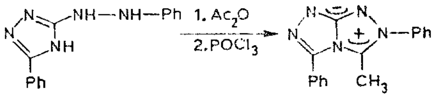


XLI

a,b,d,e = C,N ;
c,f = O,NR

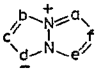


XLII

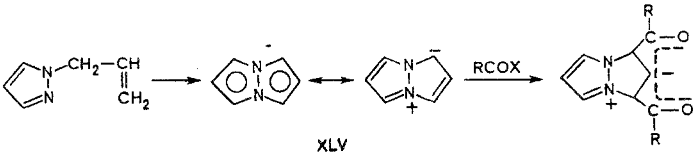


XLIII

2.1.2.3. With Two Nitrogen Atoms in Common. As mentioned above, the first mesoionic aromatic heterocycles were obtained precisely in this category. Of the 18 systems of this type (XLIV), four and their carbocyclic derivatives, which contain only nitrogen atoms as the heteroatoms, are known. These compounds can be classified as di-, tri-, and tetraazapentalenes. The simplest, colorless, and unstable (in air) diazapentalene XLV tends to give 1,3-disubstituted electrophilic substitution products and 1,7-cycloaddition products [58-64].

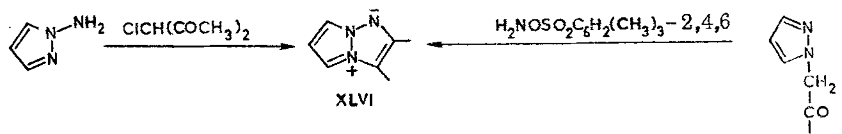


XLIV

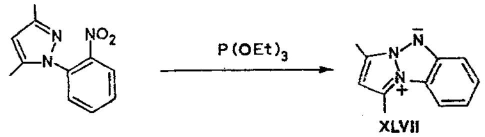


XLV

Triazapentalenes XLVI, which were obtained by the reaction of N-aminopyrazole with α-halo ketones or by N-amination of 1-phenacylpyrazole with subsequent cyclization [65], are characterized by such substitution and cycloaddition reactions. Their benzo derivatives — pyrazolo[1,2-*a*]benzotriazoles XLVII — are formed from 1-(2-nitrophenyl)pyrazoles by the action of triethyl phosphite; only the singlet intermediate nitrene leads to mesoionic products [66-71].

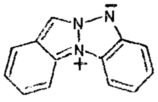


XLVI

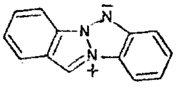


XLVII

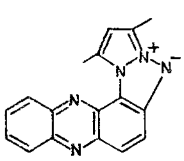
Isomeric dibenzotriazapentalenes (indazolobenzotriazoles XLVIII and XLIX) were obtained by the same method of reductive cyclization of the corresponding o-nitrophenyl derivatives with triethyl phosphite [54, 72, 73]. Blue phenazine analogs L are similarly formed or by irradiation with UV light of 1-(1-pyrazolyl)-2-azidophenazines; the pyrazole ring is opened when they are subjected to photooxidation with singlet oxygen, the 6–7 bond is hydrogenated by catalytic reduction, and the triazole ring is destroyed in the case of oxidation with peracids. They also react with acetylenedicarboxylic acid esters to give cycloaddition products with retention or opening of the pyrazolotriazole system [74–77].



XLVIII

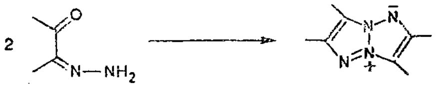


XLIX



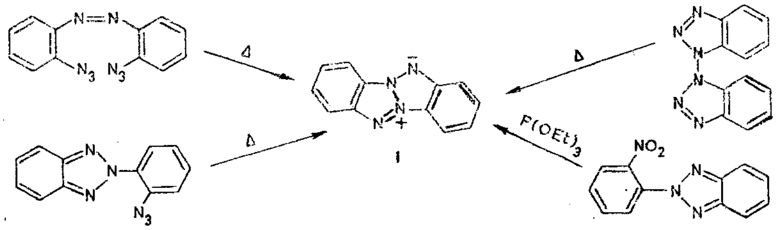
L

The first tetraazapentalenes were obtained in 1956; however tetrazocine structure was assigned to them. The error was corrected immediately after elucidation of the correct structure of dibenzotetraazapentalene I. The syntheses, properties, and structures of these compounds have been investigated quite thoroughly [78–86]. One of the methods for the preparation of derivatives LI is given below.



LI

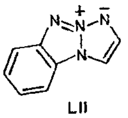
As noted above, a dibenzo derivative of 1,3a,4,6a-tetraazapentalene I was the first mesoionic heterocycle with a correctly established structure. Methods for the synthesis of this compound, which are also used for the preparation of its derivatives and analogs, are presented below [87–99].



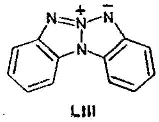
I

The structure of I was established and confirmed by means of synthetic methods, chemical properties, x-ray diffraction analysis, spectral data, and quantum-chemical calculations.

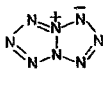
Derivatives of the isomeric 1,3a,6,6a-tetraazapentalene system were obtained in the form of benzo and dibenzo compounds LII and LIII by several of the methods presented above for the synthesis of the I system [65, 87, 98, 100].



LII



LIII

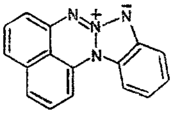


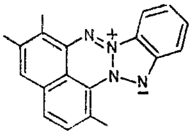
LIV

Matsumoto and co-workers are of the opinion that penta-, hexa-, and heptaazapentalenes should be stable and can be obtained [3], whereas Ramsden [5] feels that octaazapentalene LIV (pentazolopentazole), which would be an allotropic form of nitrogen, will scarcely be synthesized in the near future.

2.2. FIVE-MEMBERED HETEROCYCLES CONDENSED WITH SIX-MEMBERED HETEROCYCLES

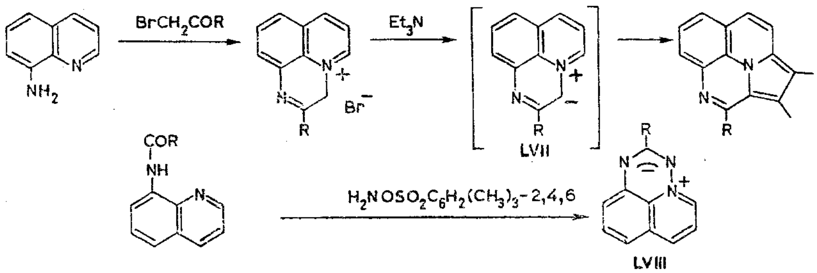
Red benzotriazolonaphthotriazine LV and blue benzotriazolonaphthotriazines LVI were obtained by reduction cyclization of the corresponding N-(o-nitrophenyl) derivatives by means of triethyl phosphite [16, 101, 102].


LV


LVI

2.3 SIX-MEMBERED HETEROCYCLES

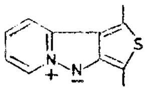
Two mesoionic heterocyclic systems LVII and LVIII were obtained from 8-aminoquinoline; LVII is unstable and was isolated in the form of cycloaddition products [103-105]. Mesoionic pyrido[2,1-b]-1,3,4-thiadiazines were obtained from 1-amino-4,6-diphenylpyridine-2-thione and α-chloro carbonyl compounds [128].

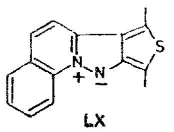


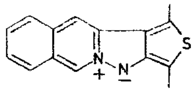
LVII
LVIII

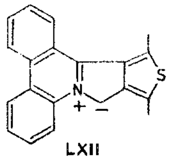
3. CONDENSED TRIHETEROCYCLES

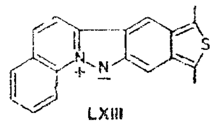
As in the case of two-ring systems, benzo derivatives of condensed triheterocycles LIX-LXIII were obtained by annelation of the thiophene ring by the action of P_2S_5 on the corresponding dibenzoyl derivatives [106, 107].* Pyrrolopyrazolopyridine LXIV is presented as a mesoionic system in a previous review [4]; however, it can be represented in the form of a

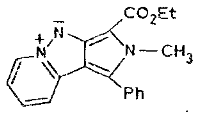

LIX

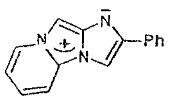

LX

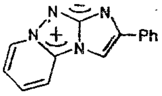

LXI

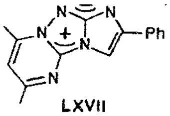

LXII

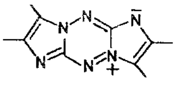

LXIII

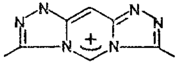

LXIV

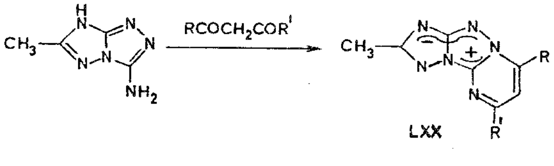

LXV


LXVI


LXVII


LXVIII


LXIX



LXX

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*Thienopyrrolobenzothiazole was similarly obtained [129].

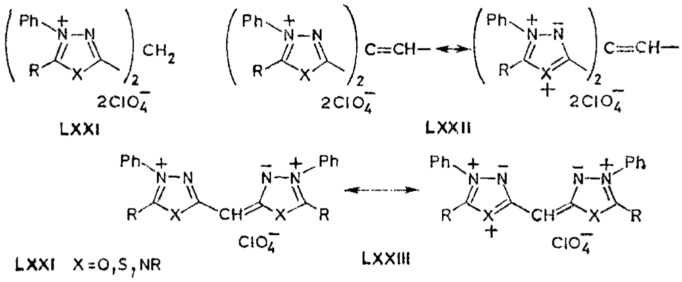
mesomeric structure with the negative charge in the side chain. Pyrido and pyrimido analogs LXV-LXVII — derivatives of unknown two-ring mesoionic azapentalenes — were synthesized by the above-indicated general method for the preparation of mesoionic condensed imidazoles. Mesoionic diimidazotetrazines LXVII, which are blue pigments, were obtained by the same method — by condensation of 3,6-diamino-1,2,4,5-tetrazine with 2 moles of α-halo ketones. An attempt to obtain mesoionic ditriazolopyrimidines LXIX by cyclization of 4,6-dihydrazinopyrimidine was unsuccessful [110], but derivatives of another triazolotriazolopyrimidine system (LXX) have been obtained [111].

II. HETEROCYCLIC BETAINE CATIONS AND METHINE DYES

Heterocyclic quaternary salts that are suitable for the preparation of methine dye usually contain an active methyl or methylene group in conjugation with an onium heterocyclic atom; conjugation between the onium atoms and the methine chain is compulsory in cationic methine dyes. Quaternary salts in which the necessary conjugation is achieved only in mesoionic (betaine cationic) mesomeric structures are described below; although these salts themselves are not purely mesoionic compounds, in the compositions of the dyes their heterorings are mesoionic, since they can be represented only by mesoionic structures with observance of the rules of conjugation in dyes (and in the compositions of symmetrical dyes only with observance of the rules of conjugation and valence).

1. UNCONDENSED HETEROCYCLES

Diquaternary salts LXXI, which were obtained [112] by methods that are known in the monocyclic series, form methine dyes via two pathways, viz., by reaction with the normal components of cyanine condensations (LXXII) and by deprotonation (LXXIII); symmetrical methylidynecyanines that are mesoionic dyes both in essence and with respect to the formal criterion, i.e., they are true mesoionic compounds, are formed in the latter case.

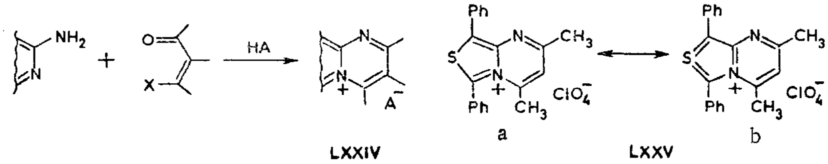


2. CONDENSED BIHETEROCYCLES

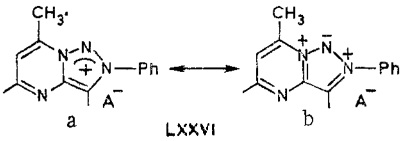
2.1. AZOLOAZINIUM QUATERNARY SALTS WITH ONE NITROGEN ATOM IN COMMON

2.1.1. With an Active Methyl Group in the Azine Ring

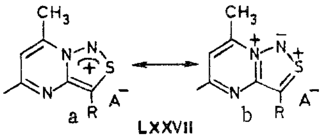
The condensation of unconjugated α-amino derivatives of nitrogen heterocycles with β-diketones and their derivatives and analogs (acetals of β-dicarbonyl compounds, β-chlorovinyl carbonyl compounds) in the presence of acid leads to pyrimidinium salts LXXIV, in which the methyl groups in the α and (or) γ positions should not be active in cyanine condensations. In fact, thiazolo[3,4-a]pyrimidinium salts LXXV do not give methine dyes [113] even despite the fact that they can formally be written in the form of structure LXXVb with a tetravalent sulfur atom.



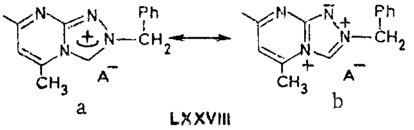
Other pyrimidinium salts of the LXXIV type (LXXVI-LXXIX), which were obtained by the same method [114-118] and have an azole ring with at least one other (unsubstituted) nitrogen atom, do form methine dyes; this is explained [119] by the existence of mesomeric betaine cationic structures of the b type.



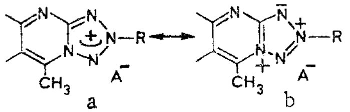
LXXVI



LXXVII



LXXVIII

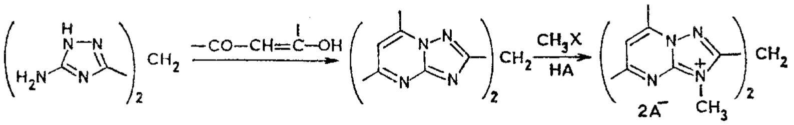


LXXIX

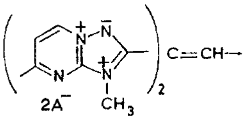
2.1.2. With an Active Methyl (Methylene) Group in the Azole Ring

The above-mentioned 1,2,3-thiadiazolo[3,4-*a*]pyrimidinium salts LXXVII with R = CH_3 form methine dyes at this methyl group, and the latter is more active than the methyl group of the pyrimidine ring; the activities of both methyl groups are explained by mesoionic structure b, and the possible structure with a tetravalent sulfur atom is also insignificant here.

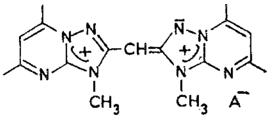
Diquaternary salts LXXX, which were obtained by the scheme presented in [120], behave, like salts LXXI, similarly to give two series of dyes (LXXXI and LXXXII); the latter, inasmuch as they are symmetrical dyes, can have only mesoionic structures.



LXXX



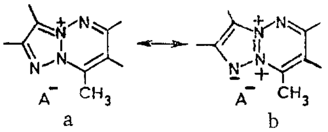
LXXXI



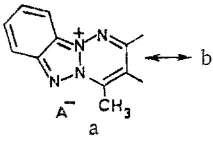
LXXXII

2.2. AZOLOAZINIUM QUATERNARY SALTS WITH TWO NITROGEN ATOMS IN COMMON

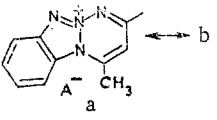
1,2,3-Triazolo[2,1-a]-1,2,3-triazinium salts LXXXIII and their benzo analogs — 1,2,3-triazino[2,1-a]benzotriazolium salts LXXXIV and 1,2,3-triazino[1,2-a]benzotriazolium salts LXXXV — were obtained by condensation of 1-amino-1,2,3-triazoles and 1- and 2-aminobenzotriazoles with β-diketones in the presence of an acid [122]. All of these salts give methine dyes owing to the existence of betaine cationic structures b.



LXXXIII



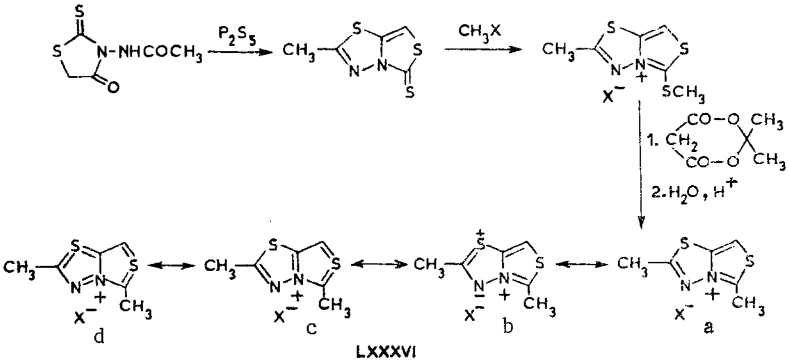
LXXXIV



LXXXV

2.3. THIAZOLO[4,3-b]-1,3,4-THIADIAZOLIUM SALTS

The activity of the methyl group of the thiadiazole ring in cyanine condensations of salts LXXXVI obtained from N-acetylaminorhodanine, which was not explained at all by Sych and co-workers [121], can be explained by means of betaine cationic structure b [119]; mesomeric structures c and d with a tetravalent sulfur atom are probably very insignificant.

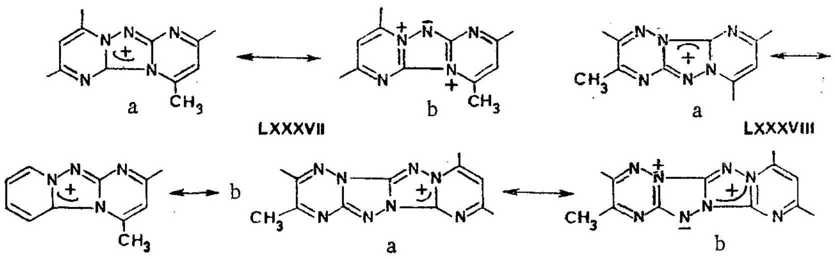


LXXXVI

3. CONDENSED TRI- AND TETRAHETEROCYCLES

3.1. AZOLOAZINIUM SALTS WITH ACTIVE METHYL GROUPS

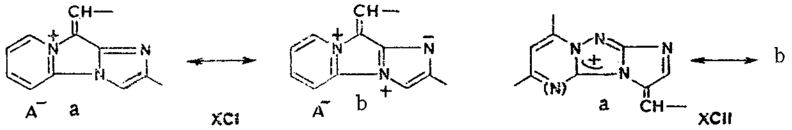
Three-ring LXXXVII-LXXXIX systems [109, 123-125] and the four-ring XC system [126] were synthesized by the method used to prepare salts of the LXXIV type. As above, the methyl groups of these salts are active as a consequence of the existence of betaine cationic structure b; the methine dyes from these salts have mesoionic structures.



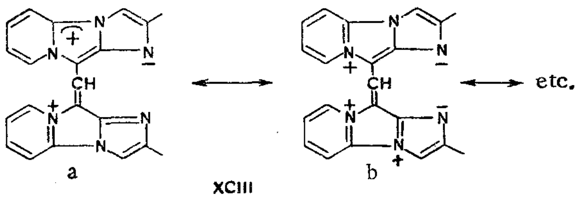
LXXXVII LXXXVIII LXXXIX XC

3.2. CONDENSED MESOIONIC IMIDAZOLES — ANALOGS OF CONDENSED AZAINDOLIZINES

The proton salts of the above-described mesoionic imidazoles LXV-LXVII give methine dyes XCI and XCII (the fragments of the dyes with the participation of the heterocycles under consideration are presented) of the same type as the dyes from indolizinium salts, the condensed aza derivatives of which are these systems. The symmetrical dyes of this series such as XCIII are purely mesoionic systems. As mentioned above, some two-ring mesoionic imidazoles such as XLII also behave similarly.



XCI XCII



XCIII

III. CONCLUSION

With respect to their nature, methods of synthesis, structures, and physical and chemical properties, mesoionic heterocycles do not, of course, differ in principle from other organic compounds and other heterocycles. However, their classification into a separate group is useful not only (as in any type of classification) as a superficial criterion. The assertion of structures of this type necessitated a certain degree of violation of the usual concepts, which always accompanies the assertion of something novel. The most valuable achievement of concepts regarding mesoionic heterocycles is precisely the novelty of the idea. As mentioned above, the idea of the mesoionic character of the heterocycles has predictive force: it makes it possible to construct new types of heterocyclic systems and opens up new divisions in the chemistry of heterocyclic systems where previously the route was closed. The materials in this review give many illustrations for this assertion. It is sufficient to recall the familiar (to the author) reactions involving the cyclization of amino and hydrazino derivatives that lead to new heterocyclic systems that were constructed on the basis of the idea of mesoionic heterocycles. The application of this idea to quaternary salts of nitrogen heterocycles made it possible to predict and obtain new types of quaternary salts that are suitable for the synthesis of methine dyes and new types of methine dyes. Despite all their inadequacies, the classical structural formulas still remain the principal instrument and guide for theoretical organic chemistry and in the case of mesoionic heterocycles are also a satisfactory means of depiction of their structures.

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