HETEROCYCLIC DIAZO COMPOUNDS AS STARTING MATERIALS IN ORGANIC SYNTHESIS (REVIEW)

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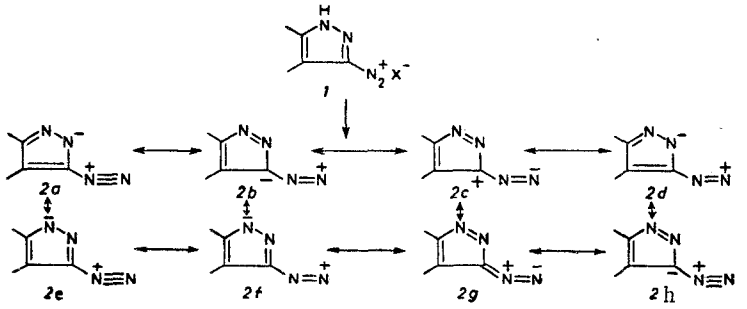
Data on the structures and reactions of heterocyclic diazo compounds that lead to the formation of new heterocyclic systems as a result of intra- or intermolecular cyclization and rearrangements are systematized.

The chemistry of aliphatic diazo compounds and aromatic diazonium salts has been examined in a number of reviews; however, considerably less attention has been directed to their heterocyclic analogs [1, 2]. The publication in recent years of a significant number of papers devoted to the use of heterocyclic diazo compounds in organic synthesis compelled us to examine in the present review the chemistry of these compounds precisely from the point of view of their application for the synthesis of heterocyclic systems. Such well-known transformations as replacement of the diazonium group, reduction, the formation of pyrazoles, indazoles, etc., were not included in the review. Principal attention here will be directed to the reactivities of heterocyclic diazo compounds, intramolecular cyclization, ring opening, and rearrangements.

1. Structure and Reactivity

The first heterocyclic diazo compound (diazotetrazole) was synthesized by Thiele [3]. It should be mentioned that the corresponding diazonium compounds 1 are usually obtained in the heterocyclic series, and diazo compounds 2 can be isolated by neutralization only in special cases (e.g., in the azole series); thus, one observes an analogy here with aliphatic diazonium ions, which are converted to diazoalkanes as a result of detachment of a proton [4]. The stabilities and reactivities of conjugated heterocyclic diazo compounds are ensured by their resonance stabilization (e.g., see structures 2a-h). Correspondingly, it may be assumed that these compounds are capable of participating in reactions as 1,2-, 1,3-, or 1,4-dipoles; reactions of this sort were also actually observed and will be described below. Their reactivities also depend on the nature of the substituent. Like the nitrogen atoms that are incorporated in the ring and display similar properties, electron-acceptor substituents promote a relatively large contribution of structures of the 2a and 2d-f type,



while electron-donor substituents promote the contribution of structures of the 2g type. In addition, heterocyclic diazo compounds are comparable to diazo oxides (the so-called diazo anhydrides or quinonediazides), whereas with respect to their behavior they occupy an intermediate position between the corresponding aliphatic and aromatic derivatives.

3-Diazoindazole was the first heterocyclic diazo compound to have its structure investigated by x-ray diffraction analysis [5]. The interatomic C—N and N—N distances in the molecules of this compound, heterocyclic α-diazo carbonyl compounds, diazomethane,

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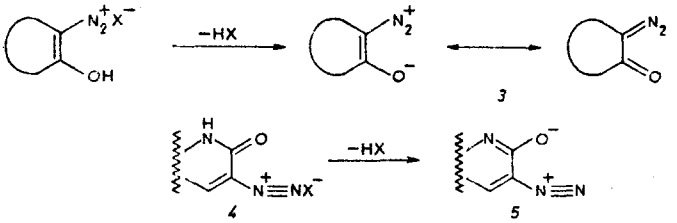
TABLE 1. Interatomic Distances (Å) in the Group

Compound	C—N	N—N
3-Diazoindazole [5]	1,338	1,110
5-Diazo-6-methoxy-6(H)uracil [6]	1,332	1,113
5-Diazocyclouridine [6]	1,308	1,12
Diazomethane [7]	1,32	1,12
Benzenediazonium chloride [8]	1,385	1,097

and aromatic diazonium salts are compared in Table 1. The length of the C—N bond in heterocyclic diazo compounds is much shorter as compared with aromatic compounds and approaches the length of the C—N bond in aliphatic diazo compounds. This suggests that it more likely has "carbanionic" dipolar character of the $>\bar{C}-\overset{+}{N}\equiv N$ type rather than $\gtrless C-\dot{\overset{+}{N}}\equiv N$ or $>C=\overset{+}{N}=\bar{N}$.

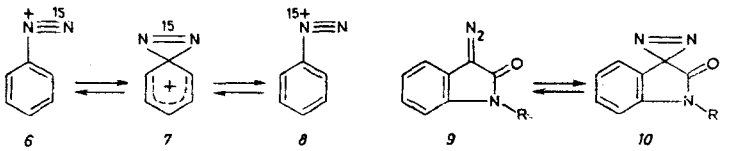
The diazotization of aminoazinones leads to diazonium salts 4, which upon neutralization are converted to dipolar diazonium azinolates 5, formally similar in a structural respect to cyclic diazo ketones 3. Some heterocyclic diazo compounds and diazo oxides do not couple with phenols; this can be explained by the small positive charge on the terminal nitrogen atom of the diazo group.



3 4 5

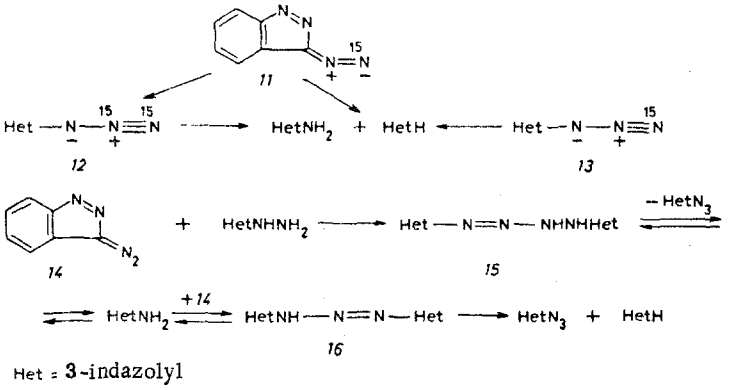
In view of possible rearrangement with exchange of the nitrogen atoms, the stability of heterocyclic diazo compounds is of particular interest. It has been established that in the synthesis of phenyl azide with $H^{15}NO_2$ both the terminal nitrogen atom and the nitrogen atom in the β position of the azido group were labeled [9]; however, migration of the label was not observed in the synthesis of a labeled azide from 2,4-dinitrophenylhydrazine [10]. Similar migration of the labels, although to a smaller extent, was noted in the synthesis of diazoacetic ester from glycine ester and $H^{15}NO_2$ [9]. Exchange between the α- and β-nitrogen atoms was also observed in the solvolysis of the benzenediazonium ion [11]; spirodiazirine 7 was postulated as an intermediate in the rearrangement in this case. Doubt was cast on the possibility of this isotopic rearrangement by the first data from NMR spectroscopy [12]; however, migration of the labeled nitrogen atom was later confirmed by the same method [13]. The hypothetical formation of a spirodiazirine as an intermediate in the rearrangement has been repudiated [14], and it is customarily assumed that in the case of arenediazonium salts the rearrangement, which takes place to slight extent, proceeds through the phenyl cation (see [15] and the literature cited therein). It has been shown that dediazotization is reversible, since a molecule of nitrogen can be incorporated in the diazo group and undergo exchange with it [16]. Recent calculations make it possible to assume that the transition state in the rearrangement of the benzenediazonium ion is a bridged structure that is more asymmetrical than structure 7; symmetrical bridged structures possibly develop in intermediate steps of nitrogen exchange [17].

Voigt and Meier [18, 19] recently succeeded in isolating and identifying the first spirodiazirine 10, which is a valence isomer of photochromic heterocyclic diazo compound 9. Similar photochromic transformations were also previously observed for diazo amides, which were converted to the isomeric diazirines [20]. A similar reversible photochemical valence isomerization is also known in the carbocyclic series [21].



6 7 8 9 10

Labeled 3-diazoindazole 11 and 3-azidoindazoles 12 and 13 are converted by photochemical elimination of nitrogen to indazole and 3-aminoindazole without isotopic rearrangement [22]. The formation of 3-azidoindazole from labeled 3-diazoindazole and potassium azide proceeds without nitrogen exchange through pentazene and pentazole intermediates [23]. Indazole, 3-amino- and 3-azidoindazole, in addition to the supposed 3-hydrazinoindazole, were isolated in the reduction of 3-diazoindazole (14); the reaction proceeds through intermediates tetrazene 15 and triazene 16 [22]. Compounds of the same types were also obtained in the diazotization of 3-aminopyrazolo[3,4-b]pyridine under the usual conditions [24]. Similar transformations were observed in the pyrazole, imidazole, and 1,2,3-triazole series. These reactions are similar to the formation of aryl azides from arenediazonium salts and hydrazine [25]. For example, 5-diazoimidazole-4-carboxamide is converted to a 5-azido derivative via this pathway, and Wiberg and co-workers [27] recently succeeded in isolating a tetrazene, which thermally either decomposed with the formation of nitrogen and hydrazine or isomerized to ammonium azide. Finally, it should be noted that some tetrazenes can undergo cyclization to tetrazoles in the presence of nucleophiles [28]. However, when there is a nitrogen atom in the ortho position of the ring, spontaneous



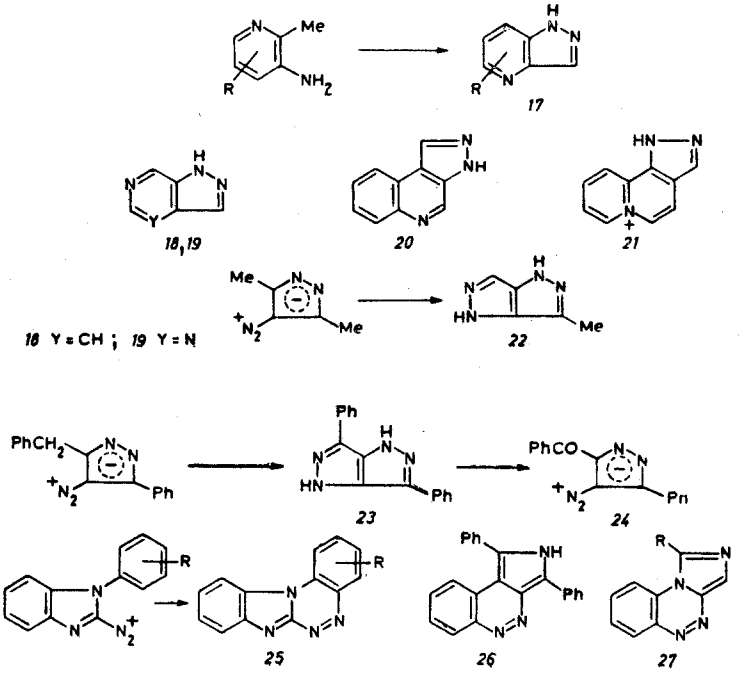
Het = 3-indazolyl

cyclization to tetrazoloazine occurs [29]. Moreover, heterocyclic hydrazines can be converted to unsubstituted heterocycles under the conditions of aza transfer in the presence of tosyl azide [30]. To uncover possible isotope exchange a similar experiment was carried out with a diazo ketone of the sym-triazolo[4,3-b]pyridazine series labeled with ^{15}N in the diazo group. This ketone did not undergo rearrangement under either thermolysis or photolysis conditions [31].

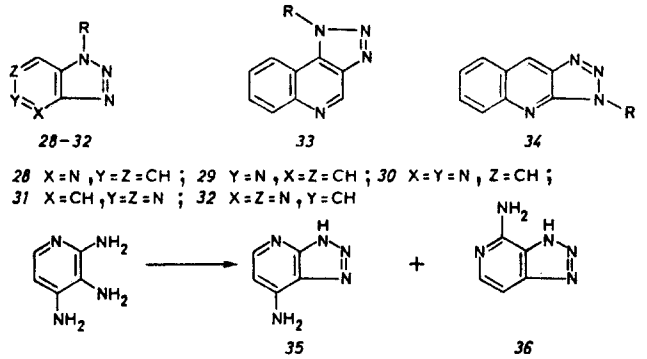
2. Intramolecular Cyclizations

Condensation of the diazonium group with an adjacent nucleophilic group is widely used in the aromatic series in the synthesis of various nitrogen heterocycles. Reactions of this type include the formation of cinnolones, indazoles, 1,2,3-benzotriazines, 1,2,3-benzotriazoles, or benzothiatriazine S,S-dioxides. Similar reactions with the participation of heterocyclic compounds, as a result of which new bonds are formed between the nitrogen atoms and carbon, sulfur, or nitrogen atoms, have also been studied in detail.

2.1 Formation of a C–N Bond. The formation of a condensed pyrazole ring is based on the reaction of a diazonium grouping with an activated methyl or methylene group. o-Methyl-substituted heterocyclic primary amines undergo intramolecular cyclization to give a condensed pyrazole ring when they are diazotized. Pyrazolo[4,3-b]pyridines 17 [32] (by direct diazotization of the corresponding amine or through a step involving the N-nitroso derivative), pyrazolo[3,4-c]pyridines 18 [33], pyrazolo[4,3-d]pyrimidines 19 [34-37], pyrazolo-[3,4-c]quinolines 20 [38], pyrazolo[5,4-a]quinolizinium salts 21 [39], and pyrazolo[4,3-c]-pyrazoles 22 [40, 41] were synthesized in this way. The latter can also be obtained by cyclization with the participation of a benzyl group: thus, 3-benzyl-4-diazo-5-phenylpyrazole in acetic acid undergoes thermal isomerization to pyrazolopyrazole 23 [42]. It is interesting to note that this compound is converted to diazopyrazole 24 when it is oxidized with chromic acid in acetic acid. In some cases similar cyclizations also take place with the participation of an o-phenyl group. Examples of this are the formation of dibenz[a,g]imidazo-[2,1-c]-1,2,4-triazines 25 [43], the intramolecular coupling of triphenylpyrrolediazonium salts with the formation of a three-ring system 26 [44], or the analogous reaction of o-(1-imidazolyl)benzenediazonium salts with the formation of imidazo[5,1-c]-1,2,4-benzotriazine 27 [45, 46].



2.2. Formation of an N–N Bond. This method is widely used in the synthesis of polyazaheterocyclic systems, particularly condensed 1,2,3-triazoles and 1,2,3-triazines. 1,2,3-Triazolo[4,5-d]pyridines 28 [47-49], 1,2,3-triazolo[4,5-c]pyridines 29 [47-53], 1,2,3-triazolo[4,5-c]pyridazines 30 [54], 1,2,3-triazolo[4,5-d]pyridazines 31 [55-58], 1,2,3-triazolo[4,5-d]pyrimidines 32 [35, 59-66], 1,2,3-triazolo[4,5-c]quinolines 33 [49], and 1,2,3-triazolo[4,5-b]quinolines 34 [49] were obtained from heterocyclic o-diamines and nitrous acid.

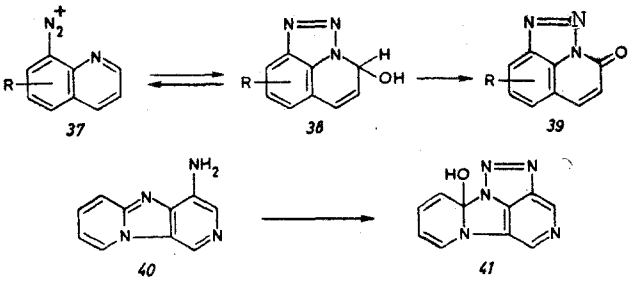


2,3-Diaminopyridine is readily oxidized by nitrous acid to the corresponding triazolopyridine [67]; however, only the 3-diazonium salt was obtained in the case of 6-chloro-3,4-diaminopyridine [68]. 4-Amino-5-methylaminopyridine is converted to the 5-N-nitroso derivative when it is treated with isopentyl nitrite or nitrous acid in aqueous solution [60]. A mixture of compounds 35 and 36 with predominance of the latter is formed in the diazotization of 2,3,4-triaminopyridine [69]; this constitutes evidence for preferred attack of the diazo group at the adjacent amino group in the 4 position.

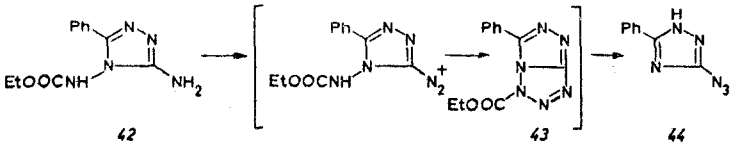
Condensed triazoles can also be obtained from heterocycles with an amino group in the peri position with respect to the NH group of the ring. Triazoloquinolines from 8-aminoquinolines [70-72], triazolobenzoxazines [73], triazolocinnolinones [74], triazoloacridones [75, 76], triazolophenoxazines [77-79] and their aza analogs [80], triazolophenothiazines [79] and the corresponding analogs [81], as well as triazolobenzacridone [82], were synthesized in this way.

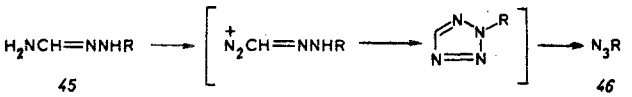
In a more detailed study of the diazotization of 8-aminoquinolines it was established that compounds of the 38 type are formed as a result of this reaction and subsequent neutralization [83]. Dehydration of 38 leads to starting diazo compounds 37, while oxidation with permanganate leads to oxo derivatives 39. A structure similar to that of 38 was proposed for cyclization product 41, which was obtained by diazotization of amine 40 with subsequent

heating of the acidic solution [84]. Compounds of the 38 type undergo ring opening in alkaline media to give benzotriazolylacrylaldehyde [83].



The diazotization of 3-amino-1,2,4-triazole 42, which leads to 3-azidotriazole 44, is a special case. However, the probable triazolotetrazole intermediate 43 could not be isolated [85]. Azide 46 is evidently similarly obtained in the diazotization of 45 [86].



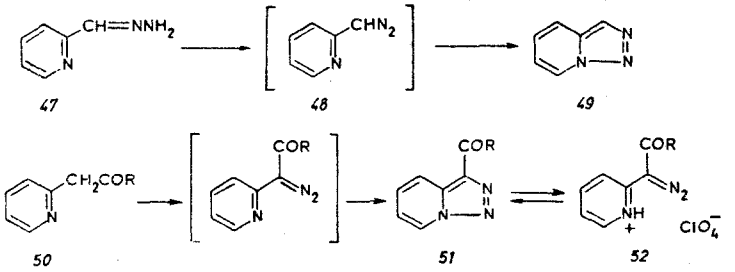


R = tetrazolo[4,5-b]pyridazinyl

When the diazonium salt reacts with heterocyclic hydrazines during the aza transfer reaction and the hydrazo group is adjacent to the nitrogen atom of the heteroring, the intermediate azide can undergo spontaneous cyclization to a condensed tetrazole [87].

Another possibility for the formation of an N–N bond is realized in the case of attack of the o-diazophenyl group on the nitrogen atom of the adjacent five- or six-membered heteroring. The synthesis of pyrazolobenzotriazines [88, 90], benzimidazolobenzotriazines [90], or 1,3,5-triazino[1,2-c]-1,2,3-benzotriazines [91] constitute examples of this type of formation of heterocyclic systems.

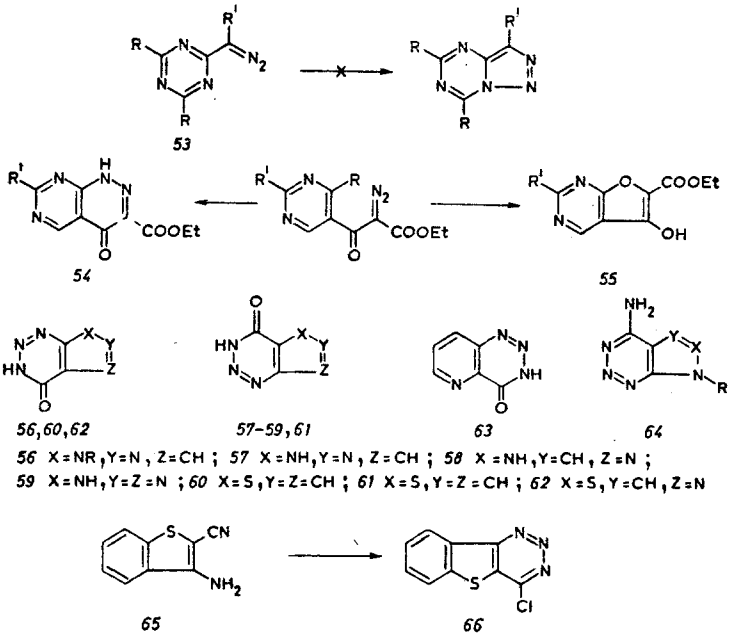
Attack by the diazo group of the side chain on the azine nitrogen atom is also possible. The oxidation of hydrazone 47 with silver oxide gives diazo compound 48, which undergoes spontaneous cyclization to 1,2,3-triazolo[3,4-a]pyridine (49) [92]. Triazoloquinolines [92] and triazoloisoquinolines [93] were similarly synthesized. An attempt to synthesize triazolopyridine 49 by diazotization of 2-aminomethylpyridine was unsuccessful. The 48 $\rightleftarrows$ 49 equilibrium has not yet been detected, and only the two-ring form exists in neutral media. Similar cyclization also occurs in the case of diazo transfer in the acyl(2-pyridyl)methane series (50 → 51) [94] or the corresponding quinoline series. However, protonation of triazolopyridines with perchloric acid in dioxane leads to ring opening to give diazo compounds 52. Salts 52 are sensitive to solvolysis and are reconverted to two-ring system 51 in the presence of ethanol or water [94].



Moreover, similar diazoalkyl-1,3,5-triazines 53 (R' = alkyl) [95] do not form condensed triazoles, while their ethoxycarbonyl analog 53 (R' = COOEt), according to our data, also exists primarily in the unclosed form. This is analogous to the azidotetrazole tautomerism in the triazine series, where only azido derivatives that do not undergo cyclization to condensed tetrazoles are known [96].

New two-ring systems (e.g., pyrimido[4,5-c]pyridazines 54 [97, 98] and furo[2,3-d]-pyrimidines 55 [98]) were recently synthesized from heterocycles with a diazo group in the side chain.

The diazotization of heterocyclic o-amino carboxamides, like the well-known conversion of o-aminobenzamides to benzo-1,2,3-triazinones [99], is the basis for the synthesis of a number of condensed 1,2,3-triazines: pyrazolo[3,4-d]-1,2,3-triazinones 56 [100], pyrazolo-[4,3-d]-1,2,3-triazinones 57 [101], imidazo[4,5-d]-1,2,3-triazinones 58 [102-105], 1,2,3-triazolo[4,5-d]-1,2,3-triazinones 59 [103, 106], thieno[2,3-d]-1,2,3-triazinones 60 [107], thieno[3,2-d]-1,2,3-triazinones 61 [108], thiazolo[5,4-d]-1,2,3-triazinones 62 [109], and pyrido[3,2-d]-1,2,3-triazinones 63 [110]. It is extremely interesting that the cyclization of 4-diazoimidazole-5-carboxamide tetrafluoroborate to give 58 proceeds much more rapidly than photochemical fluorination with replacement of the diazo group [111]. An imidine grouping may be found in the side chain in place of an amide grouping, in which case condensed aminotriazines 64 (X = CH, Y = N; X = N, Y = CH; X = Y = N) are obtained [112]. The cyclization of an o-cyano-substituted diazonium ion (65 → 66) is a special case [113].

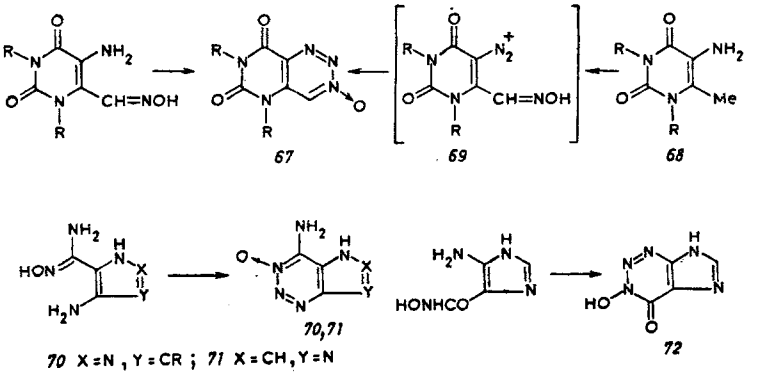


56,60,62 *57-59,61* *63* *64*

56 X=NR, Y=N, Z=CH ; *57* X=NH, Y=N, Z=CH ; *58* X=NH, Y=CH, Z=N ; *59* X=NH, Y=Z=N ; *60* X=S, Y=Z=CH ; *61* X=S, Y=Z=CH ; *62* X=S, Y=CH, Z=N

65 *66*

The reaction of the diazo group with the o-aldoximino group leads to the formation of a triazine N-oxide ring, as, e.g., in the case of pyrimido[5,4-d]-1,2,3-triazine 3-oxide 67 [114]. An oxime function is sometimes introduced in the course of nitrosation of an o-methyl-substituted amine. Thus, pyrimidine derivatives 68 are converted to condensed triazines 67 by the action of excess nitrous acid; the corresponding oxime 68 is formed in an intermediate step [115]. A similar reaction was also found in the quinoline series [38]. It is also characteristic for amidoximes, and this makes it possible to incorporate an o-amino group in N-oxides (e.g., pyrazoles 70 [101] and imidazoles 71 [116]). The diazotization of o-aminohydroxamic acids also leads to the corresponding triazine derivatives (72) [117].



67 *69* *68*

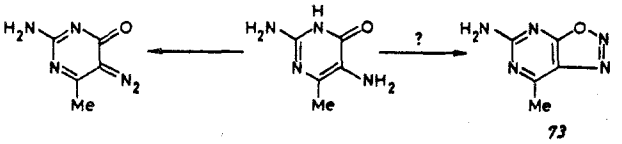
70,71

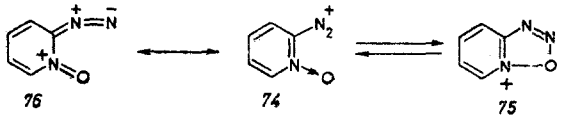
70 X=N, Y=CR ; *71* X=CH, Y=N

72

2.3. Formation of an N–O Bond. In contrast to the cases examined above, the diazotization of o-hydroxy-substituted heterocyclic amines more likely leads to diazo oxides 3 rather than to cyclization products (condensed 1,2,3-oxadiazoles). A cyclic structure has sometimes been assigned to the synthesized compounds; e.g., the formation of oxadiazolopyrimidine 73 in the diazotization of 2,5-diamino-4-oxo-6-methylpyrimidine has been reported; however, the properties of the product of this reaction correspond to a great extent to the diazo oxide structure.

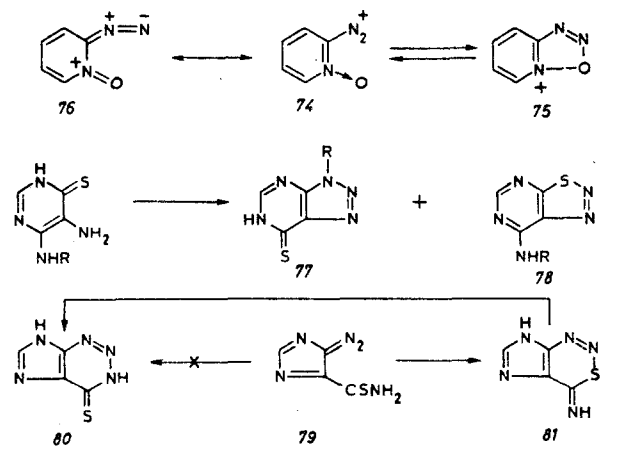
The possibility of the formation of an oxatriazole from a diazo N-oxide also seems problematical. Like the N-oxides of other azines with a diazo group in the ortho position, the 1-oxidopyridine-2-diazonium salt exists in the form of one-ring structure 74 [118, 119]. Moreover, the 2- and 4-diazonium salts of azine N-oxides are generally more stable than the diazonium salts of the corresponding azines; this is associated with the significant contribution of a canonical structure of the 76 type. However, the UV and IR spectra of tetrafluoroborates of diazonium salts obtained from the N-oxides of 2-aminopyridine, 2-aminoquinoline, and 1-aminoisoquinoline are in agreement with their cyclic structure, which is similar to structure 75 [120]. These compounds couple with β-naphthol in alkaline solutions.





2.4. Formation of an N–S Bond. In contrast to diazo ketones, their thio analogs do not exist, and o-aminomercapto-substituted heterocycles are converted to the corresponding thiadiazoles when they are diazotized. 1,2,3-Thiadiazolo[5,4-d]pyrimidines were synthesized by this method [35, 121]. An equilibrium mixture of triazolopyrimidine 77 and thiadiazolopyrimidine 78 (R = Me) was obtained in the diazotization of 5-amino-6-methylamino-4-thioxopyrimidine [59]. The same mixture is formed by the action of P_4S_{10} on the 6-oxo analog of 77 in refluxing pyridine. In this case the diazo group reacts with both the methylamino and thioxo groups. However, it should be noted that only thiadiazolopyrimidine 78 (R = H) was isolated in the diazotization of 4,5-diamino-6-thioxopyrimidine [122].

The cyclization proceeds peculiarly in the case of 4-diazo-5-thiocarboxamidoimidazole (79). In analogy with the corresponding amide, it was assumed that cyclization leads to imidazo[4,5-d]-1,2,3-triazine-4-thione (80). However, it was established that the initial product is imidazo[4,5-d]-1,2,3-thiadiazine-4-imine (81) [123, 124], which is converted to 80 in the presence of ammonia.

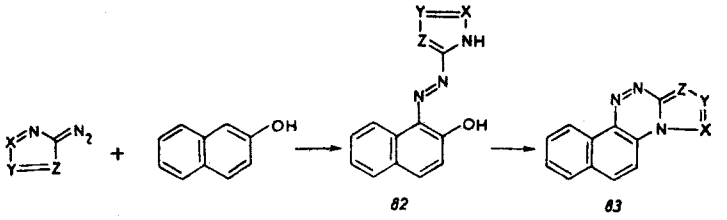


3. Intermolecular Cyclizations

Heterocyclic diazo compounds and diazonium salts are capable of coupling with phenols with subsequent cyclization of the reaction product. In addition, they can react with

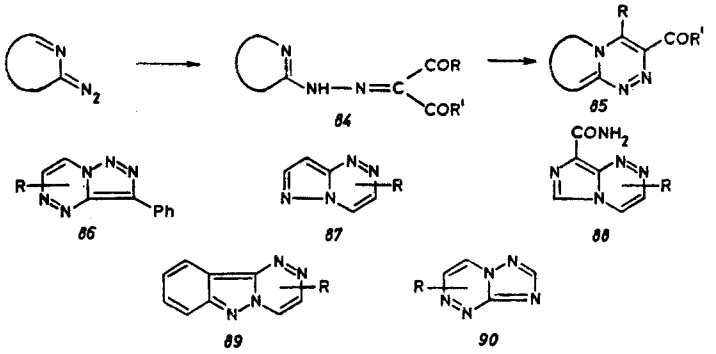
compounds that have reactive methylene groups to give hydrazones, which also undergo cyclization to give a new azaheterocycle. In the case of α-methylene carbonyl compounds the reaction can be interpreted as the addition of the diazo group to the enol double bond. Many other reactions involving addition to a carbon–carbon multiple bond are also known.

3.1. Heterocycles Obtained by Means of a Coupling Reaction. Naphthopyrazolo-1,2,4-triazines 83 (X = N, Y = Z = CH) are formed by coupling 3-diazopyrazoles with β-naphthol [125-127]. Ofitserov and co-workers [123] were able to isolate intermediate azo compounds, viz., derivatives of diazoimidazole, diazopyrazole, diazo-1,2,3-triazole, and diazotetrazole. On the basis of the experimental data it was concluded that the ease of cyclization of azo compounds 82 to naphthotriazines 83 depends on the relative basicity of the heterocycle and decreases in the order imidazole ≫ pyrazole > 1,2,4-triazole > 1,2,3-triazole > tetrazole [128]. Coupling with ring formation was used in the synthesis of polycyclic 1,2,4-triazines (e.g., indazolonaphthotriazine [129] and its analogs [130, 131]).



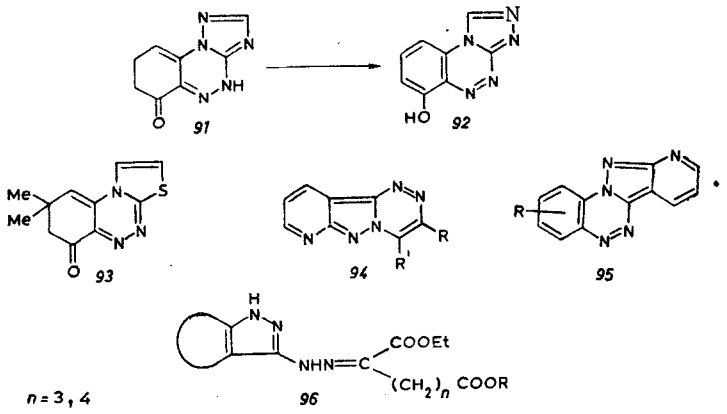
82 83

The primary products of the reaction of heterocyclic diazo compounds and diazonium salts with compounds that contain reactive methylene groups are hydrazones or enehydrazines. Attempts to isolate intermediate hydrazones of the 84 type have sometimes been successful; however, when they were heated or subjected to acid catalysis conditions, they were converted to condensed 1,2,4-triazines 85. Thus, derivatives of 1,2,3-triazolotriazine 86 or the corresponding hydrazones or a mixture of compounds of both these types were obtained from 5-phenyl-1,2,3-triazole-4-diazonium salts [132]. Pyrazolotriazines 87 are formed from pyrazole-3-diazonium salts [22, 133-135], imidazotriazines 88 are formed from 4-diazo-5-carboxamides [22], and indazotriazines 89 are formed from 3-diazoindazole [136-139].



84 85 86 87 88 89 90

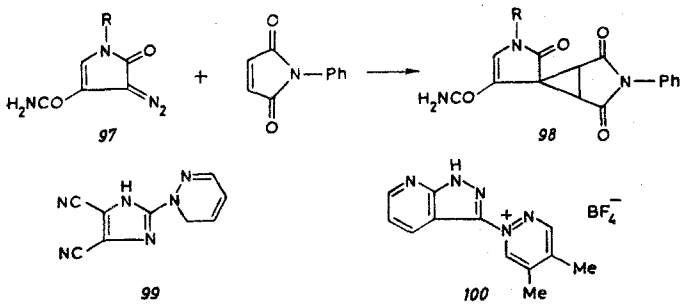
The coupling of diazotized 3(5)-amino-1,2,4-triazole with compounds that contain an active methylene group leads to derivatives of triazolotriazine 90 or its benzo analogs [140-142]. It should be noted that treatment with a hot ethanol solution of hydrogen chloride leads to aromatization of three-ring system 91 with simultaneous rearrangement to



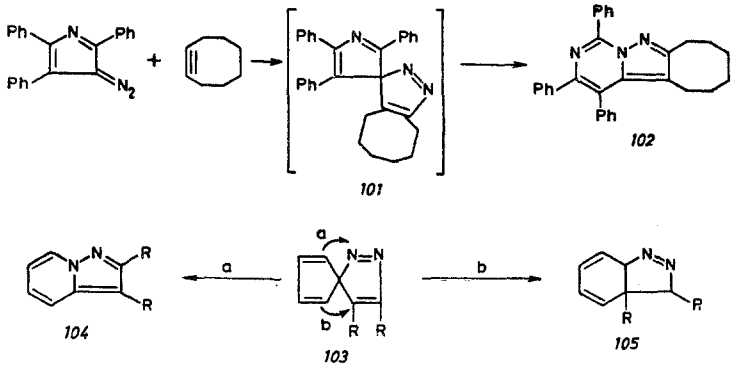
91 92 93 94 95 96

92 (an example of a retrograde Dimroth rearrangement) [140]. Diazotized 2-aminothiazoles also can give coupling products; however, Gorjan and co-workers [140] were able to realize cyclization of the latter to thiazolotriazines of the 93 type only in the case of dimedone. Polyazaheterocycles 94 and 95 were similarly obtained from 3-diazopyrazolo[3,4-b]pyridine [24]. However, some cyclic dicarbonyl compounds (such as esters of 2-oxocyclopentane- and 2-oxocyclohexanecarboxylic acid) react with diazo compounds via the mechanism of the Japp—Klingemann reaction [143] with the formation of hydrazones 96 [22, 137]. A similar transformation was observed in the case of methylacetoacetic acid [138].

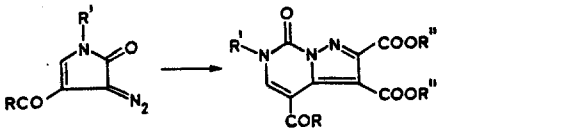
3.2. Reactions Involving the Addition of Diazoheterocycles to Multiple Bonds. Diazo compounds can undergo cycloaddition reactions as 1,2-, 1,3-, and 1,4-dipoles. For example, 3-phenylpyrazole-5-diazonium chloride adds to acrylic derivatives to give pyrazolo[3,2-c]-1,2,4-triazines 87 [134]. In the reaction of diazopyrrolinone 97 with N-phenylmaleimide the intermediate pyrazoline is converted, as a result of splitting out of nitrogen, to 98, which contains a cyclopropane fragment [144]. 3-Diazo-4,5-dicyanoimidazole reacts with butadiene as a 1,2-dipole to give pyridazine derivative 99 [145]. A similar reaction of pyrazolo[3,4-b]pyridine-3-diazonium tetrafluoroborate with 2,3-dimethylbutadiene, which leads to pyridazinium salt 100, has also been described [24]. Only the corresponding azo olefin is formed in the reaction with cis-1,2-dimethoxyethylene, which is a clearly expressed electron donor; however, a pyrazolotriazine of the 87 type was obtained from ethoxyethylene and diazopyrazole in almost quantitative yield [146]. The formation of cyclic adducts is also possible in the reaction of diazo compounds with enamines and ketene O,N-acetals [147].



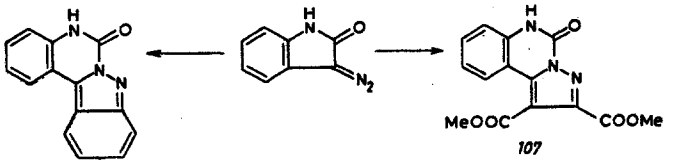
A number of examples of the reactions of diazoheterocycles with acetylene compounds are known. Diazoazoles react with ynamines [110] and very active alkynes or cycloalkynes [148] to give the corresponding azolo-1,2,4-triazines. For example, pyrazolopyrimidine 102 was obtained as a result of the reaction of 3-diazo-2,4,5-triphenylpyrrole with cyclooctyne, which proceeds as 1,3-dipolar cycloaddition [149]. The primary product of the addition (spiro compound 101) was not isolated, although it was found that it could be isolated in the case of the analogous reaction with diazocyclopentadiene. Spiro compound 101 undergoes rapid sigmatropic rearrangement only in one direction with the formation of a single reaction product, viz., 102. This process differs from cycloaddition with the participation of diazocyclopentadiene, in which intermediate spiro compound 103 undergoes rearrangement to pyrazolo[1,5-a]pyridine 104 or to indazole 105 [150, 151]. The driving force for the rearrangement is undoubtedly the formation of a stable aromatic compound with 10 π electrons (this rearrangement is sometimes called the van Alphen rearrangement [152]).



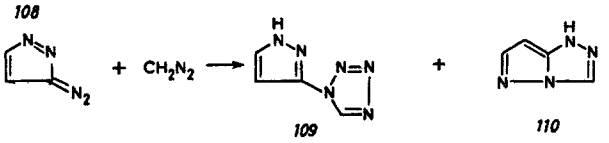
The reaction of diazopyrrolinones with acetylenedicarboxylates leads to pyrazolo[1,5-c]-pyrimidines 106, again through intermediate spiro derivatives [144, 153]. Three-ring systems 107 were obtained in the same way from 3-diazooxindole [154]. In the course of addition to dehydrobenzene the initially formed spiro compound evidently is ultimately converted to indazoloquinazoline derivative 108 [97]. Finally, 3-diazopyrazole undergoes 1,3-dipolar cycloaddition with diazomethane to give pyrazolyltetrazole 109 [155], the structure of which was established by means of x-ray diffraction analysis. It was later ascertained [156] that a small amount of pyrazolo[5,1-c]triazole (110) is simultaneously obtained.



106



108 107



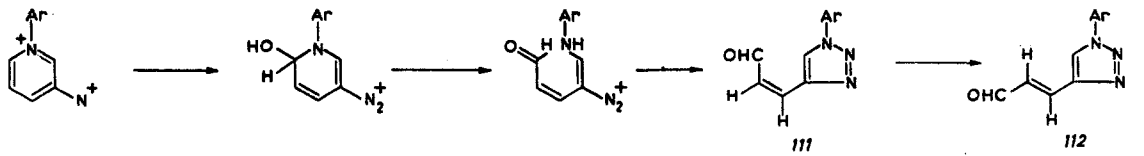
109 110

4. Reactions with Splitting Out of a Diazo Group

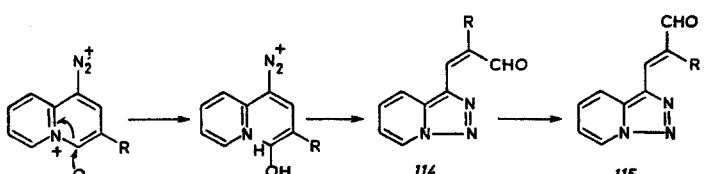
As a result of thermal or catalytic splitting out of a diazo group with simultaneous ring formation, heterocyclic diazonium salts can be converted to new heterocyclic systems. In analogy with the reactions of carbocyclic diazo compounds, transformations of this type are sometimes called the Graebe–Ullmann or Pschorr reaction, to which several reviews have been devoted. Many condensed heterocycles [157] (e.g., carbazoles, carbolines [158, 159], dibenzofurans, dibenzothiophenes, phenanthridines, azaphenanthrenes [160], etc.) have been synthesized by this method. On the other hand, the decomposition of heterocyclic diazo compounds may also lead to the formation of hetarynes (see an earlier review [161]).

5. Thermal and Photochemical Rearrangements of Heterocyclic Diazo Compounds and Diazonium Salts

5.1. Chemical and Thermal Initiation of the Rearrangements. Several types of rearrangements of diazoheterocycles are known. The first type involves ring opening and subsequent recyclization of the diazo derivatives of quaternized heterocycles. Thus, as a result of diazotization, 1-aryl-3-aminopyridinium salts are converted to 1,2,3-triazolylacrylaldehydes [162, 163]; the initially formed cis form 111 is readily isomerized to the



111 112

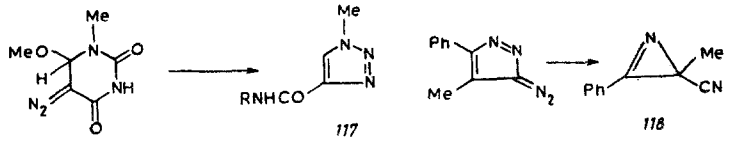


113 114 115

more stable trans isomer 112. A similar rearrangement is also characteristic for diazotized 1-aminoquinolizinium chloride (113). A diazonium salt was obtained only when nitrosylsulfuric acid or pentyl nitrite was used [164]. Diazotization with nitrous acid in dilute aqueous solutions leads to a neutral compound to which a furazan structure was tentatively assigned [164]. It was later [165] demonstrated that the product of this reaction, which is also peculiar to analogs of 113, is actually 1,2,3-triazolo[1,5-a]pyridine (115). In the presence of traces of acid cis isomer 114 is rapidly converted to the more stable trans isomer 115 [165, 166]. It should be noted that the cis configuration is always retained under experimental conditions that do not promote isomerization, and cis aldehyde 114 is thus always obtained initially.

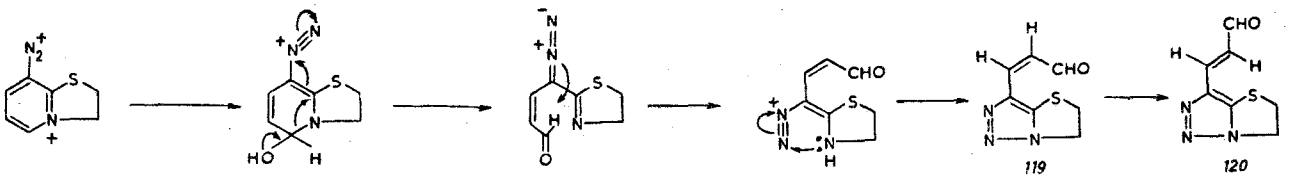
A rearrangement of a different type due to thermal initiation occurs in the case of 5-diazo-6-methoxy-1-methyl-1,6-dihydrouracil (116) [170, 171] or 5-diazocyclouridine [172, 173], which are converted to triazoles 117. The mechanism of this reaction was established by means of a double label. In the case of diazouracil intermolecular transfer of the substituent (OMe) from C_6 to C_2 is followed by ring opening at the N_1—C_2 bond and the development of a new heteroring with the formation of a bond between N_1 and the diazo group [168].

Another type of thermal transformation was observed in the case of 3-diazopyrazoles. For example, the principal product of the pyrolysis of 3-diazo-4-methyl-5-phenylpyrazole [250°C (60 mm)] is azirine 118 [146].



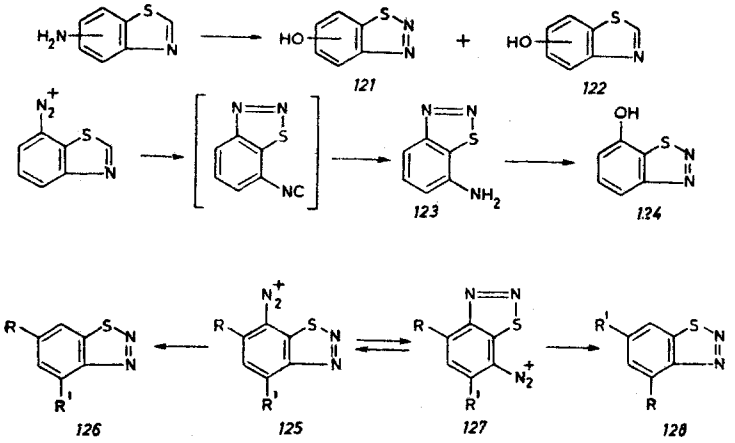
116 117 118

A new ring can be formed as a result of attack of the endocyclic nitrogen atoms or the sulfur atom by the diazonium group. The diazotization of 8-aminodihydrothiazolo[3,2-a]-pyridinium with isopentyl nitrite in aqueous acetic acid gives a mixture of cis- (119) and trans-(thiazolo[2,3-e]-1,2,3-triazolyl)acrylaldehyde (120) in equal ratios [171]. The basis of this transformation is the addition of a hydroxide ion to the electron-deficient pyridinium system with subsequent ring opening and reaction of the endocyclic nitrogen atom with the diazo group.



Depending on the ratio of the concentrations of nitrous acid and the substrate, hydroxybenzothiazoles 122 or hydroxy-1,2,3-benzothiadiazoles 121 are formed in the diazotization and hydrolysis of 5- and 6-aminobenzothiazoles [172]. In particular, hydroxy-1,2,3-benzothiadiazoles 121 were obtained when excess nitrous acid was used. The mechanism of this rearrangement has not been studied; however, there can be no doubt that opening of the thiazole ring and the subsequent formation of a condensed thiadiazole fragment occur in this case. 7-Aminobenzothiazole behaves differently: 7-aminobenzothiadiazole (123) was obtained in the reaction of this compound with one equivalent of nitrous acid. When excess nitrous acid is added, the amino group is converted to a hydroxy group to give 124 [172]. During this rearrangement opening of the thiazole ring is followed by electrophilic attack of the diazonium group on the endocyclic sulfur atom. A new rearrangement of diazonium salts was detected as a result of further studies in this area [173]. Diazotization of substituted 7-amino-1,2,3-benzothiadiazoles with subsequent splitting out of a diazo group by means of hypophosphorous acid or by means of the Sandmeyer reaction may lead both to the expected normal reaction products 126 or to rearrangement products 128 [173]; the substituents play an important role in this case. If there is no substituent in the 4

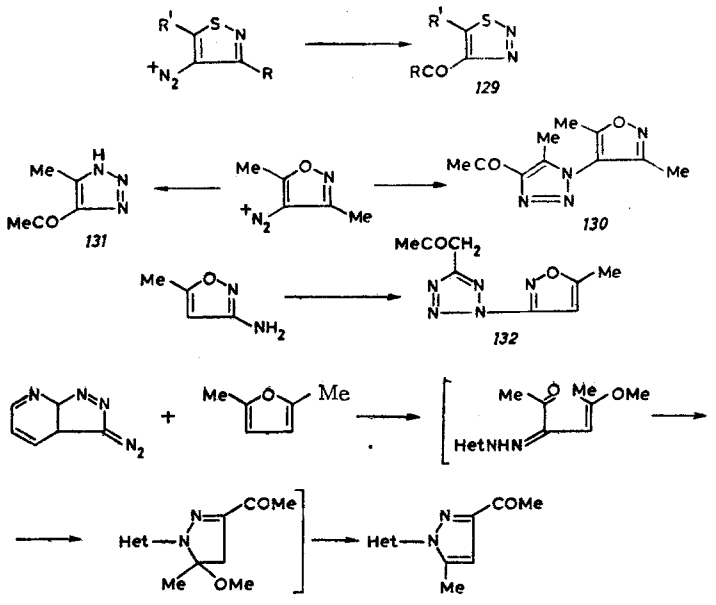
position, the presence of any substituent in the 6 position gives rise to a rearrangement, which to a considerable extent is a consequence of a steric effect. Due to this effect the diazonium group approaches the endocyclic sulfur atom sufficiently closely, and this facilitates the 125 → 127 rearrangement.



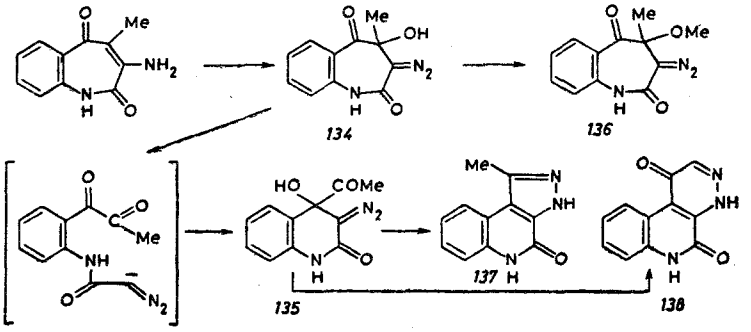
Another type of rearrangement, the mechanisms of which has not been proved rigorously, has been found for diazoisothiazoles. While diazotized 5-amino-3-methylisothiazole reacts with thiourea in the usual way to give the corresponding thio compound, which then undergoes conversion to the disulfide, 4-amino-3-methylisothiazole gives 4-acetyl-1,2,3-thiadiazole (129) under these conditions [174]. 4-Aminoisothiazole and its 5-methyl analog also undergo the reaction.

Isoxazolyl-1,2,3-triazole (130) was obtained instead of the expected cyano compound in the diazotization of 4-amino-3,5-dimethylisoxazole with subsequent treatment with potassium cyanide and copper sulfate [175]. This result can be explained by the formation of an intermediate triazene. Similarly, when 3,5-dimethylisoxazole-4-diazonium salt is heated in the presence of copper sulfate and sulfuric acid, it is converted to triazole 131 [176]. The diazotization of 5-methyl-3-aminoisoxazole with half the equivalent amount of sodium nitrite in 10% hydrochloric acid leads to the corresponding triazene rather than the diazonium salt. When the triazene is dissolved in a warm alkaline solution, it gives isoxazolyltetrazole 132 [177]. A similar reaction, which includes ring opening with the subsequent formation of pyrazole 133, occurs in the reaction of 3-diazopyrazolo[3,4-b]-pyridine with 2,5-dimethylfuran [24].

A number of interesting transformations were observed in the benzazepine series. The principal product of the reaction of 3-amino-2H,5H-4-methyl-6,7-benzazepine-2,5-dione with



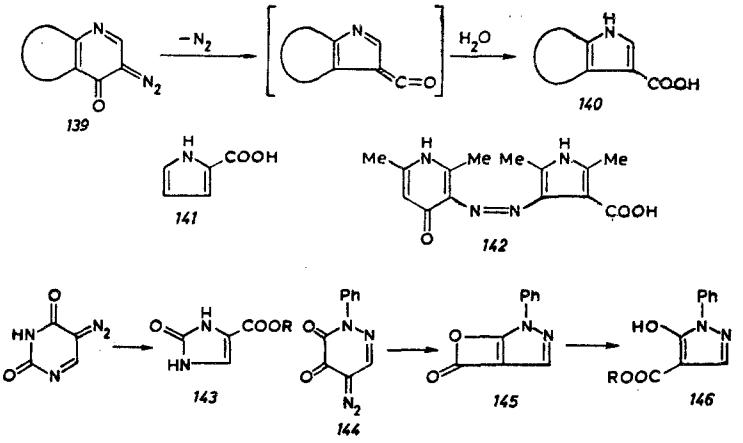
nitrous acid is benzazepine 134. This compound undergoes rearrangement to quinoline derivative 135, which is also formed in small amounts directly during the diazotization [178]. Diazo compound 136 was isolated in the case of diazotization in a mixture of methanol and acetic acid. In addition, three-ring system 137 is obtained in the hydrogenation of 135, evidently as a result of reduction of the diazo group and subsequent cyclization of the intermediate hydrazine. The thermal rearrangement of diazoquinoline 135 gives a carbostyril derivative, whereas it is converted almost quantitatively to 138 under acid catalysis conditions [178].



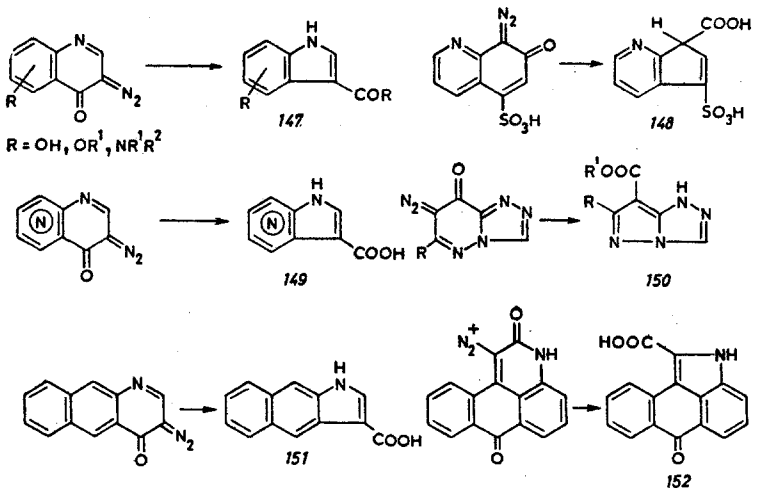
5.2. Photochemical Rearrangements. Heterocyclic compounds that are converted to diazo oxides by diazotization are, as a rule, capable of undergoing photochemical isomerization via a scheme analogous to the Wolff rearrangement for diazo ketones (139 → 140). The reaction proceeds with ring contraction; a competitive process is the formation of singlet α-keto carbenes, the rate of reaction of which with nucleophilic agents is higher than the rate of rearrangement [18, 19, 179, 180]. These photochemical rearrangements of diazo ketones can be used in the synthesis of various derivatives of indole, azaindoles, and pyrrole. The mechanisms of the thermal, photochemical, and catalytic Wolff rearrangements have been the subject of a number of studies [181], which led to the concept of the formation of intermediates of two types, viz., keto carbenes and oxirenes. However, in the pulse photolysis of 9,10-diazophenanthrone neither a carbene nor an oxirene was found among the four intermediates [182]. An oxirene has been detected only in the photolysis of acyclic α-diazo carbonyl compounds, whereas attempts to prove its presence for other diazo ketones were unsuccessful (see [183-186] and the literature cited therein).

3-Diazo-2-pyridone undergoes isomerization to pyrrole-2-carboxylic acid (141) [187], while 3-diazo-4-pyridone undergoes isomerization to pyrrole-3-carboxylic acid [188]. However, the 2,6-dimethyl analog of the latter diazo ketone adds to pyrrole — the rearrangement product — to give azo compound 142 [189]. 5-Diazouracil undergoes photochemical conversion to 2-oxo-4-imidazoline-4-carboxylic acid or its derivatives 143 [190] together with small amounts of uracil.

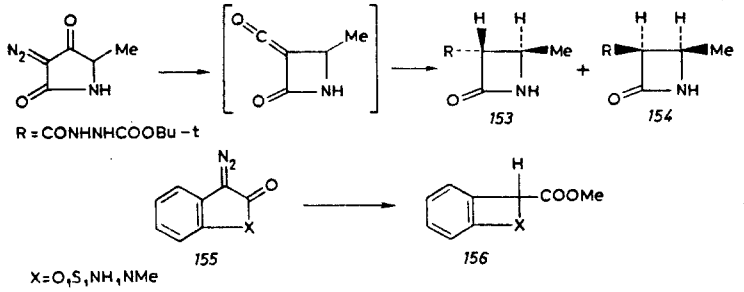
The ring contraction of 4-diazo-5,6-dioxotetrahydropyridazine 144 is a special case. When the solid form of this compound is stored for 10 days in the dark without access to moisture, it is converted to reactive lactone 145, which can subsequently react with nucleophiles to give pyrazolecarboxylic acid or its derivatives 146 [191].



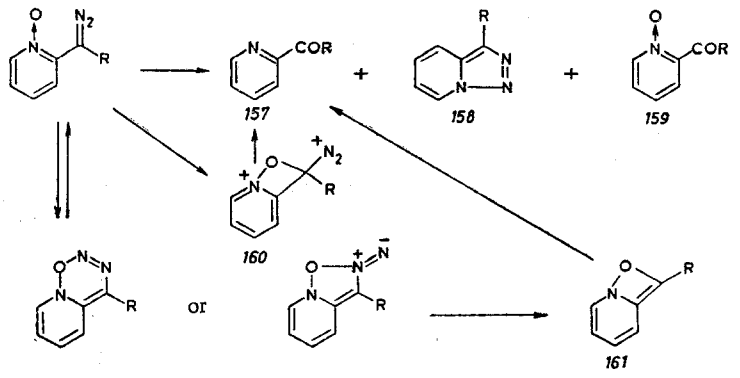
As other examples of ring contraction one can cite the photochemical formation of indoles 147 [187-189, 192-194], cyclopentapyridine 148 [187, 188], azaindoles 149 [187, 195-197], benzimidazoles [188], benzothiazoles [187], benzotriazoles [188, 198], pyrazolotriazole 150 [199, 200], and a number of other heterocycles (e.g., 151 [177, 201] and 152 [202]).



Similarly, a mixture of cis- and trans-β-lactams 153 and 154 was obtained in the photolysis of 3-diazo-5-methylpyrrolidine-2,4-dione in the presence of tert-butyl carbazate [203, 204]. This rearrangement is a new and rather general method for the synthesis of β-lactams, but its stereoselectivity is extremely low. Ring contraction was also studied in the case of 5,5-disubstituted analogs; for example, irradiation of an asymmetrically substituted pyrrolidinedione leads to the formation of two epimeric β-lactams [205]. In the series of diazo derivatives 155 the ability to undergo rearrangement decreases on passing from sulfur-containing (X = S) to oxygen- and nitrogen-containing compounds [206, 207]. Rearrangement to four-membered heterocycles is not characteristic for compounds of the latter two types.



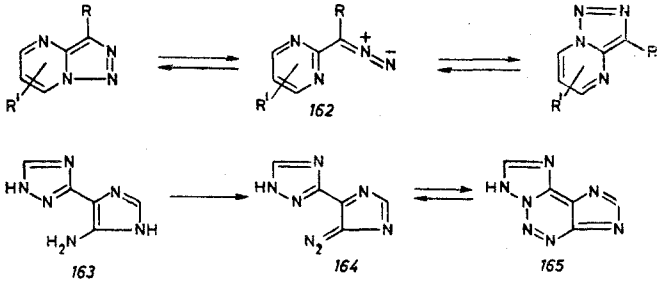
In the course of the photorearrangements of some diazo oxides in the presence of sensitizers triplet carbene reacts primarily with detachment of a hydrogen atom. Thus a compound of the 150 type was obtained from diazo-sym-triazolopyridazine in the absence of a sensitizer, while 6-methyl-8-hydroxy-sym-triazolo[4,3-b]pyridazine is formed in the presence of a sensitizer [208].



In the case of thermal or photochemical decomposition (1-oxido-2-pyridyl)diazomethane is converted mainly to 2-acylpyridine 157 together with small amounts of triazolopyridine 158 and 2-acylpyridine 1-oxide 159 [209]. The latter two substances are probably formed as a result of a bimolecular reaction, while 157 is possibly produced through intermediate structures of the 160 or 161 type.

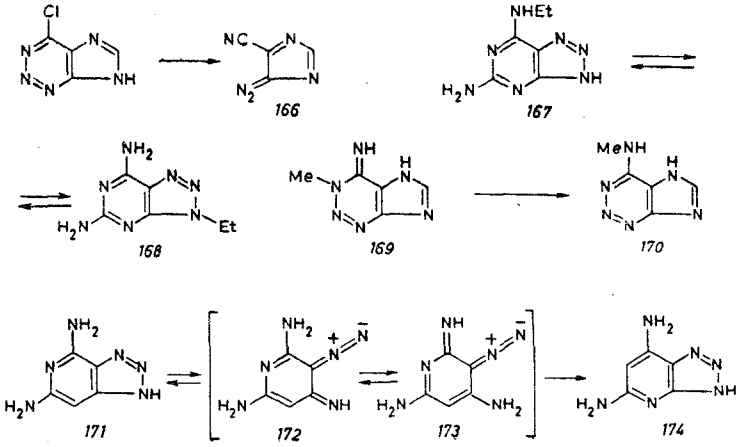
5.3. Rearrangements of 1,2,3-Triazoles and 1,2,3-Triazines (Latent Diazonium Compounds). Some transformations of 1,2,3-triazoles and 1,2,3-triazines that are condensed with a heterocycle are similar to those observed for a number of one-ring analogs and their benzo derivatives that are capable, when they are heated or subjected to acid catalysis, of giving intermediate diazo or diazonium compounds as a result of cleavage of the heteroring.

Thus it is assumed that ring–chain tautomeric transformation precedes the thermolytic cleavage of condensed 1,2,3-triazoles (e.g., triazolopyridines [210, 211]). The existence of an equilibrium between the diazoalkylideneamine and 1,2,3-triazole was first demonstrated for 1,2,3-triazolo[1,5-a]pyrimidines, for which Tennant and Vevers [212] were able to detect intermediate diazo compound 162 at high temperatures. Amine 163, in the diazotization of which a mixture of tautomers 164 and 165 is formed [213], is worthy of mention. Only the protonated form of diazo compound 164 is present in trifluoroacetic acid, while only 165 is present in DMSO or 2-methoxyethanol. Both forms exist simultaneously when trifluoroacetic acid is added to a solution in DMSO. In the case of related tetrazole analogs, in addition to this equilibrium, one should reckon with the possibility of azido-tetrazole tautomerism.



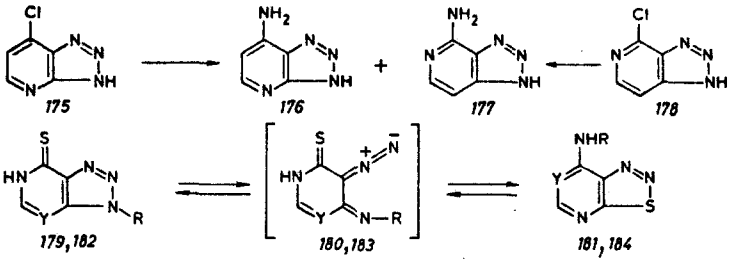
The lability of the triazine ring was demonstrated in the case of imidazo[4,5-d]-1,2,3-triazine, which undergoes rearrangement to diazoimidazole 166 when it is heated in water [214].

It has been established that 167 and 168 are interconvertible [215]. Although this rearrangement hypothetically proceeds through an intermediate diazo compound, attempts to trap the latter were unsuccessful. The 169 → 170 rearrangement may also take place similarly [216]. The conversion of triazolopyridine 171 to the isomeric triazolopyridine 174, which takes place under rather severe conditions, is also explained by the existence of intermediate diazo compounds 172 and 173 [47].



The corresponding amine 176 and a small amount of rearrangement product 177 are formed when 7-chlorotriazolopyridine 175 is heated with an ethanolic solution of ammonia (at 150°C for 19h) [217]. A mixture of 176 and 177 was also obtained from the isomeric chloro derivative 178. These facts constitute evidence for the formation of diazo compounds similar to 172 and 173 during the rearrangement. A mixture of the expected compound and the rearrangement

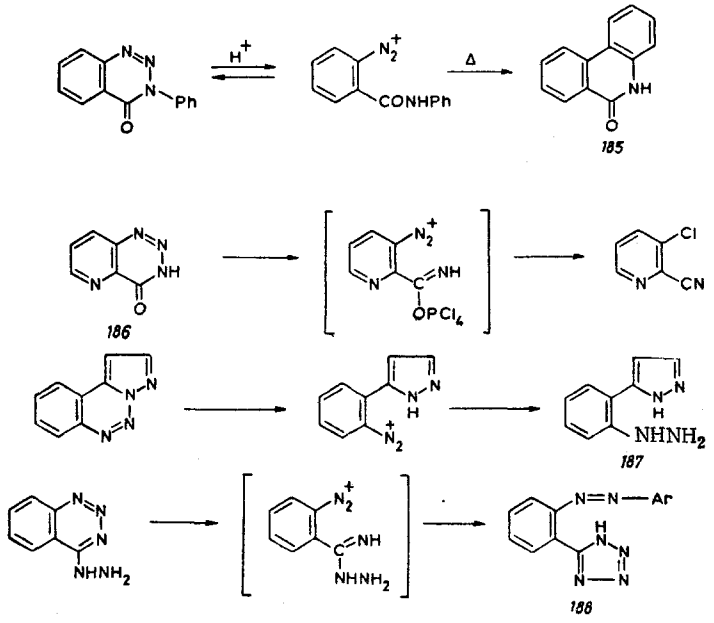
product was also obtained in the thionation of chloro derivative 175. It was demonstrated by a special experiment that thione 179 (R=H) undergoes partial rearrangement to thiadiazolopyridine 181 (R=H) in refluxing propanol and vice versa. In this case also the rearrangement is explained by the formation of intermediate diazo compound 180 [217]. The 2,3,5-Tri-O-benzoyl-β-D-ribofuranosyl analog of 179 in solution at room temperature exists in equilibrium with isomeric form 181. When the solution is heated, the equilibrium is shifted to favor this form [218]. A similar thermal rearrangement was observed for triazolopyrimidines 182, which are converted via an equilibrium process to thiadiazolopyrimidines 184 [59, 219, 220].



179–181 Y=CH; 182–184 Y=N

The disintegration of the triazole ring of condensed triazoles under the influence of acidic reagents is also linked with the formation of an intermediate diazonium ion and subsequent attack of the solvent or other reagent on the resulting carbonium ion [221-227].

In strongly acidic solutions one observes the formation of a diazonium ion from 1,2,3-triazine derivatives and coupling of this ion with phenols. The decomposition of some benzotriazinones in phosphoric acid was used to obtain 6-phenanthridones 185 [228-230] and phenanthridines [231]. The mechanism of these reactions is similar to the mechanism of the Pschorr reaction [232]. The conversion of pyrido[3,2-d]-1,2,3-triazin-4-one (186) to 2-cyano-3-chloropyridine by the action of phosphorus pentachloride can also be explained by the formation of intermediate diazo compound 110. Hydrazine 187 was obtained in the reduction of pyrazolobenzotriazine with tin(II) chloride in hydrochloric acid; the intermediate



is evidently a diazonium salt [88]. Finally, a diazonium salt, which is converted to the tetrazole fragment in 188 as a result of coupling with phenol and cyclization of the side chain, is formed instead of the expected azide in the nitrosation of 4-hydrazinobenzo-1,2,3-triazine in an aqueous medium [233].

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