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Tetrazoles

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Abstract. A systematic account is given of the latest data on the methods of synthesis, physicochemical properties, and practical applications of tetrazoles. New results obtained in the study of the electronic structures, acid–base properties, tautomerism, reactivities, and thermal stabilities of tetrazoles are discussed. The bibliography includes 369 references.

I. Introduction

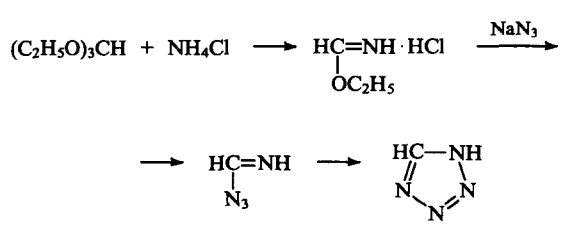
The development of the chemistry of tetrazoles during the last decade has been largely associated with the wide-scale employment of these compounds in medicine,[1–12] biochemistry,[13–17] agriculture,[18–20] and photography,[21,22] and also as components of systems for the recording of information.[23–25] Novel [26–29] methods of synthesis of substituted tetrazoles have been developed during these years and existing methods have been significantly improved.[30–35] As a result of this, tetrazoles, which had been difficult to obtain and were rather exotic, became the subject of detailed investigation and in many instances their practical applications were recommended. New results obtained in the study of the electronic structures,[36–40] acid–base properties,[41–43] tautomerism,[44] reactivities,[45–47] and thermal stabilities[48–50] of tetrazoles are of great interest. Original studies published up to 1981 have been described schematically in other reviews.[46,51] The latest data on methods of synthesis, physicochemical properties, and practical applications of tetrazoles are discussed below.

II. Methods of synthesis of tetrazoles

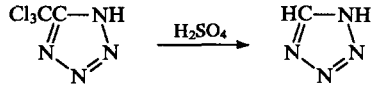
1. Tetrazole

Several methods of synthesis of tetrazole are known: the interaction of hydrocyanic acid with hydrazoic acid, the interaction of ethyl formate with sodium azide and ammonium chloride in acetic acid, the diazotisation of 5-aminotetrazole in the presence of reductants, the oxidative degradation of mono- and di-substituted tetrazoles, and certain others.[51]

Among these methods, the commonest involve the diazotisation of 5-aminotetrazole and the interaction of ethyl orthoformate with sodium azide. In the latter case, the reaction evidently proceeds via the formation of the iminoester hydrochloride and its subsequent conversion into tetrazole on treatment with sodium azide.[52]



The electrochemical reduction of 5-trichloromethyltetrazole is known to afford a low yield of tetrazole (~16%).[53] On the other hand, according to our data, tetrazole is formed in 75% yield on heating 5-trichloromethyltetrazole in 85% sulfuric acid.



The synthesis of a tetrazole containing a ^{13}C carbon isotope atom in the ring has been described recently.[54]

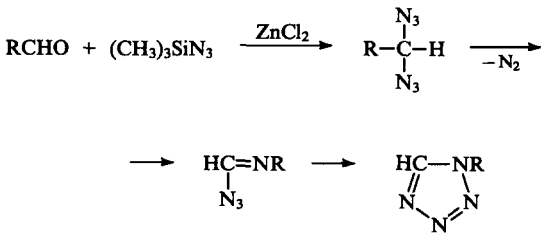
2. 1-Substituted tetrazoles

The choice of synthetic methods for 1-substituted tetrazoles is limited. The main procedure again involves addition of hydrazoic acid to isonitriles. Together with this procedure, use is also made of coupling reactions between diazonium salts and diformylhydrazine or the interaction of imidoyl chlorides, obtained from monosubstituted formamides, with hydrazoic acid.[51] Among the new methods of synthesis of 1-substituted tetrazole, mention should be made of the reaction of aldehydes with trimethylsilyl azide (TMSA)[55] and of amines with ethyl orthoformate and sodium azide.[56–59] In the former case,[55] the interaction of an aldehyde with TMSA leads to the initial formation of a diazide which is then converted into an imidoyl azide by scission of a nitrogen molecule and a rearrangement.

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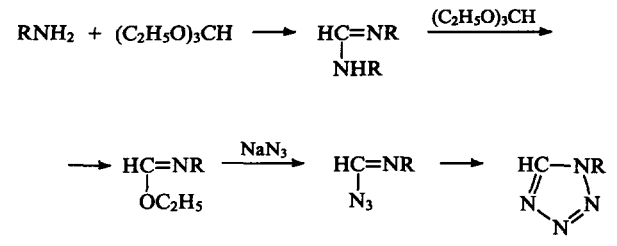
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The imidoyl azide cyclises to the 1-substituted tetrazole.



The mode of reaction depends on the aldehyde : TMSA ratio. In the presence of a threefold excess of TMSA, 1-substituted tetrazoles are formed, while for a reactant ratio ranging from 1 : 1 to 1 : 1.5 the products are disubstituted tetrazoles.

One of the most promising methods of synthesis of 1-substituted tetrazoles involves the reaction of amines with ethyl orthoformate and sodium azide. This method may be regarded as universal, since aliphatic and aromatic amines having different structures can be used for the preparation of tetrazoles. It is believed[58] that 1-substituted tetrazoles are formed in accordance with the following scheme:



1-Substituted tetrazoles can also be obtained by alkylating tetrazole. This reaction will be examined in detail in the discussion of the chemical properties of tetrazoles.

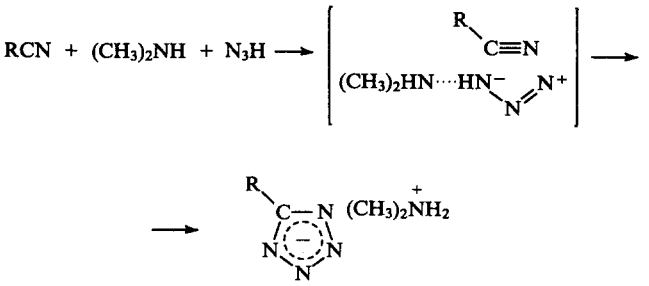
3. 2-Substituted tetrazoles

The development of simple and effective methods of synthesis of 2-substituted tetrazoles is one of the problems in the chemistry of tetrazoles of greatest current interest. As before, the only method of synthesis of 2-substituted tetrazoles involves the alkylation of tetrazole.[47,51] On the other hand, we should bear in mind that, although a wide variety of 2-substituted tetrazoles may be obtained in the alkylation of tetrazole, the application of this method usually entails difficulties in the separation of the isomeric 1- and 2-substituted tetrazoles formed as a result of the reaction.

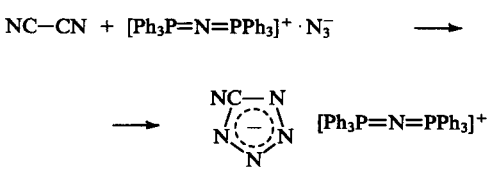
4. 5-Substituted tetrazoles

The commonest method of synthesis of 5-substituted tetrazoles involves the reaction of nitriles with salts of hydrazoic acid.[51] Both the simplest aliphatic and aromatic nitriles and nitriles with a complex structure, including those containing N-, O-, and S-heterocyclic substituents, may be used for such purposes.[60-68] The most suitable solvents for such reactions are dimethyl formamide[51] and butanol.[69]

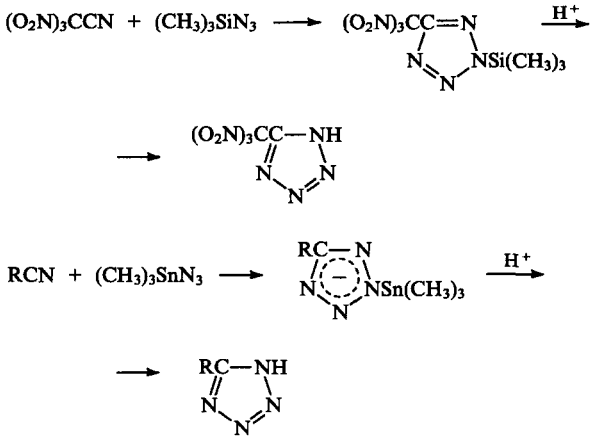
It was postulated previously that the interaction of nitriles with ammonium azides is accompanied by the formation of an imidoyl azide as a result of nucleophilic attack of the azide ion on the carbon atom of the nitrile group; the imidoyl azide cyclises to the tetrazole.[70] However, subsequently it was established in the study of the kinetics of this reaction that 5-substituted tetrazoles are formed via a 1,3-dipolar cycloaddition mechanism. In this process, the dipolarophile is the nitrile, while the hydrogen-bonded complex of the amine with hydrazoic acid serves as the 1,3-dipole.[71,72]



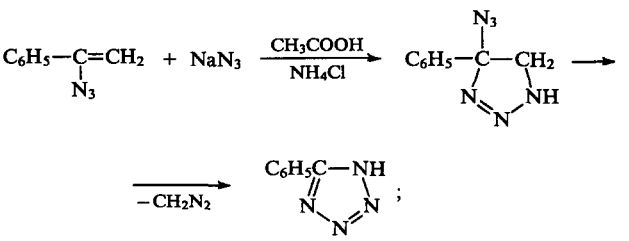
On the other hand, the possibility of the formation of 5-substituted tetrazoles via a two-stage mechanism is not ruled out. This mechanism apparently operates for substrates in which the nitrile group is linked to a powerful electron-accepting substituent, for example for trifluoro- and fluorodinitroacetonitriles[73-75] and also for oxalodinitrile.[76] It is therefore appropriate to note that oxalodinitrile reacts at a high rate with $[Ph_3P=N=PPh_3]^+N_3^-$ affording 5-cyanotetrazole in 96% yield.[76]



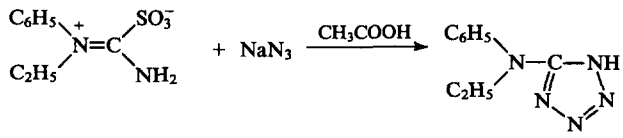
Instead of the salts and complexes of hydrazoic acid, trimethylsilyl azide[29,74] as well as trimethyl- and tributyl-stannyl azides[77,78] may be employed in the reaction with nitriles. In such cases, 1-trimethylsilyl- and 1-trimethyl(butyl)stannyl-5-R-tetrazoles are formed in the first stage, being converted into 5-R-tetrazoles on acid hydrolysis.



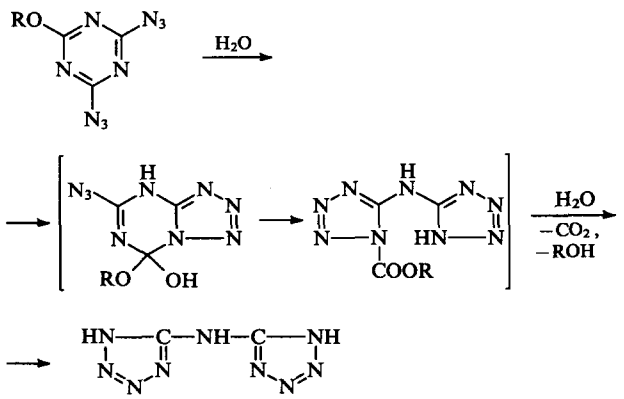
One should include among the novel methods of synthesis of 5-substituted tetrazoles the reaction of 1-azido-1-phenylethene with sodium azide in acetic acid or in dimethylformamide (DMF),[27] i.e.



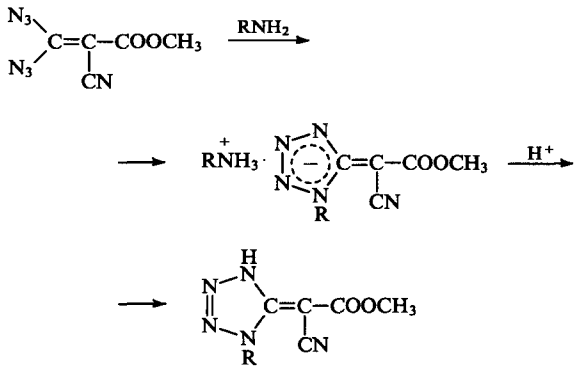
as well as the interaction of aminoiminomethanesulfonic acids with sodium azide in acetic acid.[28]



An interesting method of synthesis of di(tetrazol-5-yl)amine has been proposed.[79] When 6-alkoxy-2,4-diazido-1,3,5-triazines are heated in water, a ring carbon atom and the alkoxy-group linked to it are eliminated, which leads to di(tetrazol-5-yl)amine.



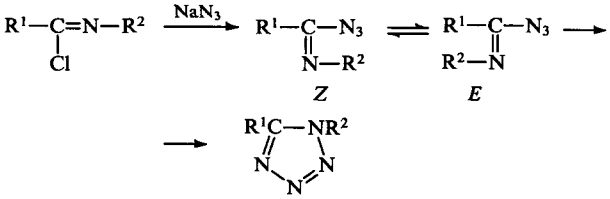
The synthesis of 5-substituted 4,5-dihydrotetrazoles from methyl 3,3-diazido-2-cyanoacrylate and ammonia or amines in a satisfactory yield has been reported recently.[80,81]



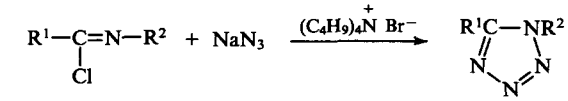
R = H, Alk

5. 1,5-Disubstituted tetrazoles

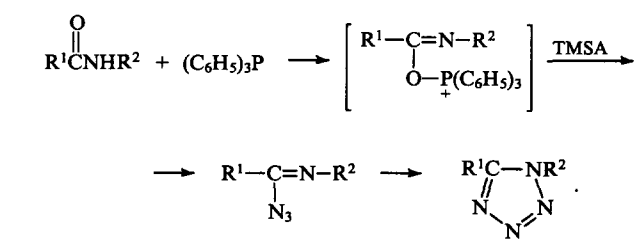
The reactions of imidoyl chlorides with hydroazoic acid or inorganic azides is again one of the most commonest methods of synthesis at 1,5-disubstituted tetrazoles. This method is universal and can be used to synthesise 1,5-disubstituted tetrazoles containing a wide variety of functional groups.[82–91] The kinetics and mechanism of this reaction have been investigated.[92,93] It has been shown that the interaction of an imidoyl chloride with sodium azide involves the formation in the first stage of a mixture of the (*Z*)- and (*E*)-conformers of the imidoyl azide in which only the (*E*)-conformer is converted into the tetrazole.



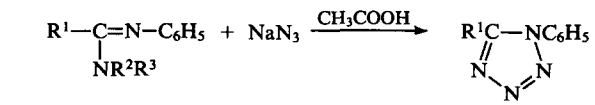
In the synthesis of 1,5-disubstituted tetrazoles from imidoyl chlorides and hydrazoic acid, one should bear in mind that certain precautions must be taken in working with hydrazoic acid, which is highly toxic and explosive. The use of inorganic azides instead of hydrazoic acid enables these difficulties to be avoided to a large extent, but, owing to the limited solubility of these reagents, the reaction must be carried out in DMF.[94,95] Other solvents—dry dioxane, ethanol, or acetone—are less effective.[96–99] The addition of water to the reaction mixture makes it possible to increase somewhat the solubility of alkali metal azides, but, owing to the hydrolysis of the imidoyl chloride, the yield of 1,5-disub-stituted tetrazoles diminishes.[100] This conflict was resolved with the aid of phase transfer catalysis. It was shown that imidoyl chlorides react at a high rate with sodium azide in the methylene chloride (chloroform)–water two-phase system in the presence of phase transfer catalysts (tetrabutylammonium bromide, 5-butyl-2,3-diphenyltetrazolium bromide, or hexa-decyltributylphosphonium bromide). Under these conditions, tetrazoles are formed in 87%–92% yields.[33–35]



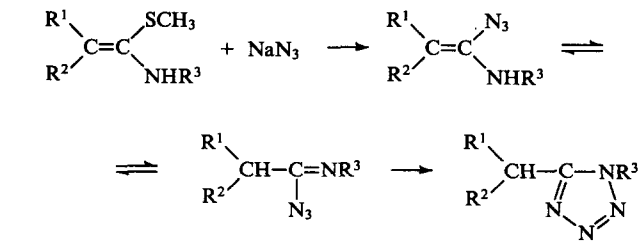
It has recently been reported that trimethylsilyl azide may be used in the reaction with imidoyl chloride instead of hydrazoic acid or inorganic azides.[101] It has been stated[78] that trimethylsilyl azide has been used successfully in the synthesis of 1,5-disub-stituted tetrazoles from amides and triphenylphosphine. The reaction evidently proceeds in accordance with the following mechanism:



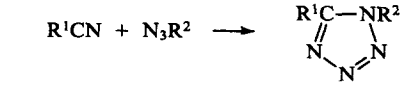
A convenient method of synthesis of 1,5-disubstituted tetrazoles has been proposed by Gaponik et al.,[102] who found that the reaction of amidines with sodium azide in acetic acid results in the formation of the corresponding tetrazoles in a high yield.



Finally, 1,5-disubstituted tetrazoles may be obtained from *S,N*-acetals of ketene on heating the latter with sodium azide in dimethyl sulfoxide.[26]



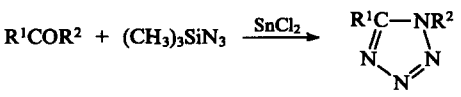
One of the fairly thoroughly investigated methods of synthesis of 1,5-disubstituted tetrazoles involves the reaction of nitriles with aliphatic and aromatic azides.



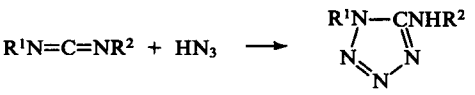
Nitriles having different structures have been used to obtain 1,5-disubstituted tetrazoles.[103-105] The process is significantly accelerated when the reaction is carried out at an increased pressure (10 kbar).[30,31,106,107]

The transition state in the reaction of nitriles with organic azides is formed by the interaction of the HOMO of the azide and the LUMO of the nitrile.[108] This conclusion agrees with experimental data and also accounts for the influence of steric factors on the reactivity of nitriles and organic azides.

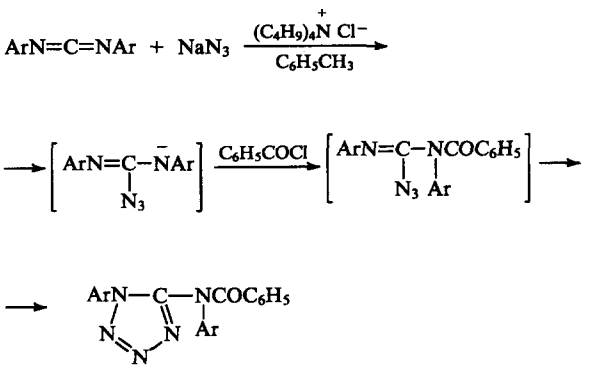
The reaction of ketones with hydrazoic acid is very important for the synthesis of 1,5-disubstituted tetrazoles.[51] The mechanism and synthetic possibilities of this reaction have been investigated in very great detail. It has been shown that ketones of various structures, including steroid ketones, may be used in the synthesis of 1,5-disubstituted tetrazoles. The reaction is carried out in the presence of catalysts such as sulfuric or trichloroacetic acids,[109,110] boron trifluoride etherate,[111,112] and titanium tetrachloride.[113] For a long time, the principal limitation of the method was the need to use hydrazoic acid. These difficulties were overcome by using trimethylsilyl azide with tin chloride[114] or trifluoroacetic acid[115] instead of hydrazoic acid.



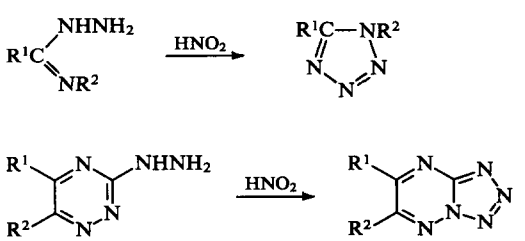
Yet another common method of synthesis of 1,5-disubstituted tetrazoles involves the reaction of carbodiimides with hydrazoic acid.[116-118]



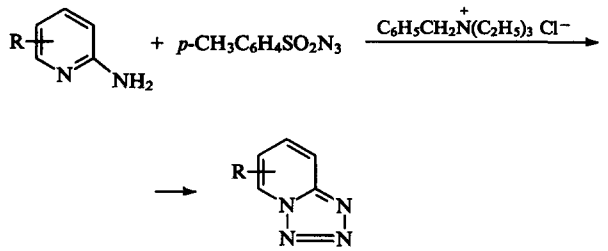
If the reaction is carried out under the phase transfer catalysis conditions in the presence of benzoic acid chlorides, then sodium azide may be used instead of hydrazoic acid.[32]



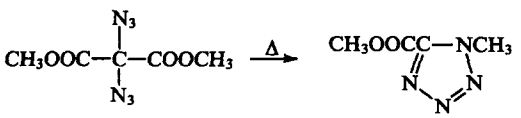
1,5-Disubstituted tetrazoles may be obtained by treating hydrazides,[119] 4-hydrazino-1,2,3-triazines,[120] or 3-hydrazino-1,2,4-triazines[121] with hydrazoic acid.



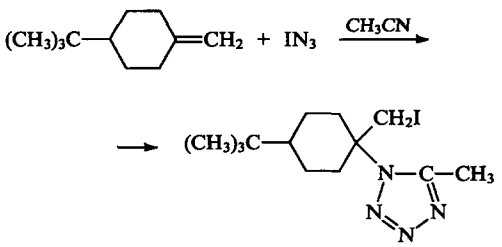
An interesting method of synthesis of annelated tetrazoles by the interaction of 2-aminopyridine or 2-aminoquinoline with toluene-*p*-sulfonyl azide under phase transfer catalysis conditions has been proposed.[122]



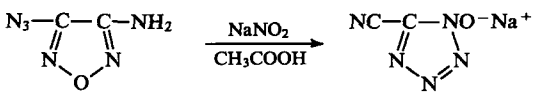
Finally, mention should also be made of a series of methods of synthesis which have so far been used to a limited extent. In the first place, this includes the reaction of isocyanates with sodium azide[123] or trimethylsilyl azide[124] and the thermal rearrangement of 5-azido-1,2,3-triazoles[125,126] and the diesters of 3,3-diazidomalonic acid.[127]



This group of syntheses also includes the addition of iodine azide to norbornene[128] and 4-(*tert*-butyl)-1-methylenecyclohexane[129] acetonitrile.

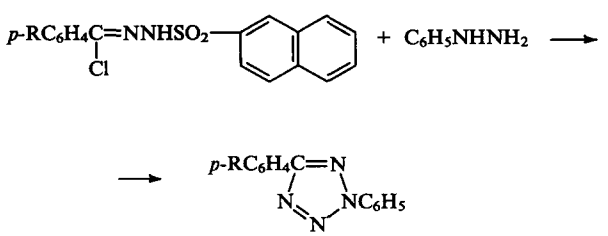


Several further methods of synthesis of 1,5-disubstituted tetrazoles have been proposed recently: the reaction of 1,3-oxazinium salts with sodium azide,[130] the reaction of benzotriazole with glyoxal and sodium azide,[131] and the diazotisation of 3-amino-4-azido-1,2,5-oxadiazole.[132]



6. 2,5-Disubstituted tetrazoles

The methods of synthesis of 2,5-disubstituted tetrazoles have been developed inadequately. Not even one fundamentally new method of synthesis of these compounds of a general character has been proposed during the last decade. Nevertheless, the reaction of imidoyl chlorides with phenylhydrazine is noteworthy.[133]

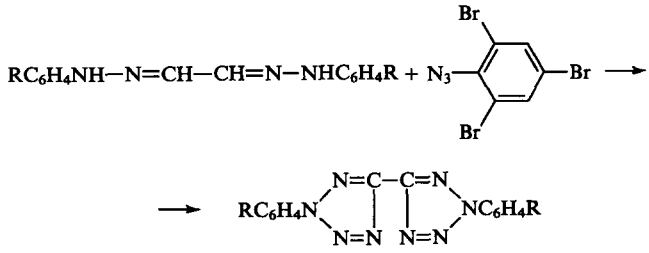


R = H, CH_3, OCH_3, NO_2

N-(Naphthalenesulfonyl)benzohydrazides were used to synthesise the imidoyl chlorides.

A novel method of synthesis of 2-aryl-5-(2-aryltetrazol-5-yl)tetrazoles, based on the reaction of glyoxal bisarylhydrazones with 2,4,6-tribromoazidobenzene, has been proposed (Scheme 1).[134]

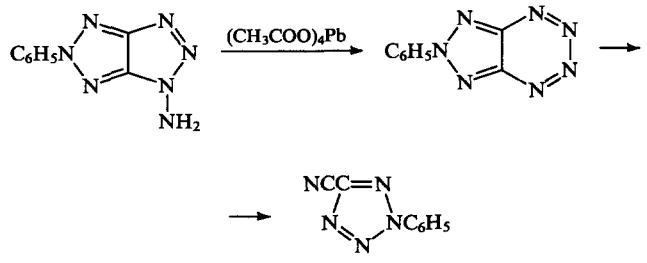
Scheme 1



R = H, OCH_3, Br, Cl

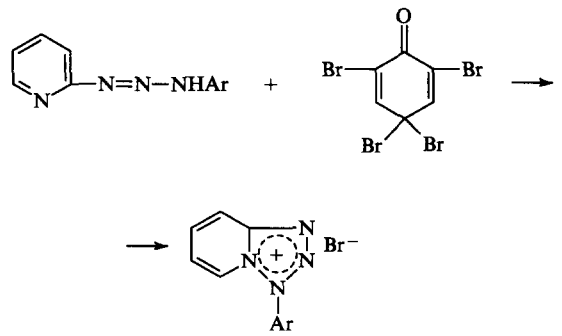
Finally, mention should be made of an interesting example of the conversion of condensed 4-amino-2-phenyl-1,2,3-triazolo-[4,5-*d*]-1,2,3-triazole into 5-cyano-2-phenyltetrazole on treatment with lead tetraacetate (Scheme 2).[135]

Scheme 2

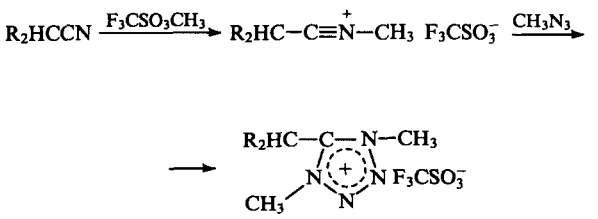


7. Tetrazolium salts

Isomeric 1,2,5-, 1,3,5-, 1,4,5-, and 2,3,5-trisubstituted tetrazolium salts are known. The synthesis of these compounds has been reviewed.[136] Studies published after 1986 are considered below. The syntheses of a series of 1,2,5-trisubstituted tetrazolium salts by oxidising 3-aryl-1-(2-pyridyl)triazenes with 2,4,4,6-tetrabromocyclohexa-2,5-dien-1-one have been described.[137,138]



The alkylation of 1,5- and 2,5-disubstituted tetrazoles is a convenient method of synthesis of tetrazolium salts.[136] It has been shown recently[139] that 1,4,5-trisubstituted tetrazolium salts are formed in a satisfactory yield in the alkylation of 1,5-disubstituted tetrazoles by dialkyl sulfates or alkyl iodides. The above tetrazolium salts have also been obtained by the successive treatment of nitriles with methyl trifluoromethanesulfonate and methyl azide.[140]



The oxidation of formazans having different structures with potassium permanganate in an organic solvent–water two-phase system leads to the corresponding tetrazolium salts in a high yield. A significant feature of this reaction is the fact that the role of the phase transfer catalyst is assumed by the tetrazolium hydroxide formed in the first stage of the reaction—in the oxidation of the formazan at the interface.[34,141,142]

The synthesis of mesoionic tetrazoles has been described.[143–145]

III. Physicochemical properties

1. Electronic structure

Nonempirical quantum-chemical methods have been used successfully during the last decade to study the electronic structure of tetrazoles. Attention has been concentrated on the problem of prototropic tautomerism in the solution of which an ab initio method was employed. The total energies of 1*H*- and 2*H*-tautomers of tetrazoles have been calculated in terms of the 6-31G** and 6.311+G(2*d*, 2*p*) basis sets. It follows from these data that the 2*H*-tautomer is more stable in the gas phase.[146,147] The vertical ionisation potential of the 2*H*-tautomer of tetrazole, calculated by quantum-chemical methods, agrees with the experimental value obtained by photoelectron spectroscopy.[148] It is noteworthy that the higher stability of the 2*H*-tautomer in the gas phase is indicated by the results of quantum-chemical calculations for the radical-cations of the two prototropic tautomers, carried out by the semiempirical CNDO/2 method, and also by mass-spectrometric data.[149,150] On the other hand, calculations by the modern semiempirical MNDO method indicate a greater stability of the 1*H*-tautomers of tetrazole and 5-fluorotetrazole in the gas phase.[36,37]

Objectively, the choice of the basis set does not play a fundamental role in the analysis of the prototropic tautomerism of tetrazole by a nonempirical method. However, the situation changes on passing to the protonated tetrazole (the tetrazolium cation). Here one should bear in mind that, in the calculation of the energy of the protonation of tetrazole in terms of a minimal basis set, unduly high values are obtained. It follows from the calculation that the tetrazolium cation containing protons in the 1- and 4-positions in the heterocycle is the most stable and that the relative stability of this tautomer diminishes by 29.3 kJ mol^{-1} on passing from the STO-3G basis set to the 6-31G**/6-31G basis set.[38,151] A similar analysis has been carried out for the protonation of 1-methyl- and 2-methyl-tetrazoles, in which the basicity centre is also the N(4) atom of the heterocycle according to the ab initio (6-31G) calculation.[152]

The extensive application of quantum-chemical methods made it possible to obtain valuable information not only about the prototropic tautomerism of tetrazoles but also about many other interesting questions. Thus a topological analysis of the structures of complexes of tetrazole with Li^+, Na^+, K^+, and Al^{3+} has been carried out by an ab initio method. The possibility of different relative dispositions of the heterocyclic ligand and the metal ion in space has been demonstrated.[40]

Modern semiempirical methods have also been used successfully in the analysis of the electronic structures of tetrazole and its derivatives. It has been shown that the MNDO method describes adequately the electronic structures of tetrazoles and that the application of this method is sometimes preferable to the use of the ab initio method in terms of a minimal basis set.[153]

At the same time, it has been noted that the method yields enthalpies of formation which are too low by 83.8 kJ mol^{-1}: 230.5 and 248.0 kJ mol^{-1} for 1*H*- and 2*H*-tetrazoles respectively.[36]

We may list a further several studies in which the electronic structures of tetrazoles have been investigated. Thus a study has been made[154,155] of the electronic structures of various alkyl- and alkenyl-tetrazoles (MNDO). The proton affinities of tetrazole and substituted tetrazoles have been calculated.[156] The azidoazomethine–tetrazole equilibrium has been analysed[36] and the structure of a dipolar diazonium tetrazolate has been considered in another study.[157] One should include here also the recently published results of an ab initio calculation of the potential energy profile for the Dimroth rearrangement of 1-substituted 5-aminotetrazoles[158] and the stability of the relatively unstable electronic states of tetrazole[159] as well as the results of semiempirical calculations of the electronic parameters of the reactants and products in the alkylation reactions of salts of 5-substituted tetrazoles (CNDO, CNDO/2),[160,161] the exhaustive alkylation of isomeric *N*-alkyltetrazoles,[162] and the aminomethylation of *N*-alkyl-5-aminotetrazoles (CNDO/2).[163]

Quantum-chemical calculations have been used effectively for the interpretation of the UV spectra of 1,4-dihydro-5*H*-tetrazoles (CNDO/S-CI),[164] the ^{15}N NMR spectra of tetrazole (MNDO), *N*-alkyltetrazoles (INDO/S-SOS),[165,166] *N*-aminotetrazoles (INDO),[167,168] and tetrazolopyridines (INDO/S-SOS),[169] and also of the mass spectra of the isomeric methyltetrazoles (CNDO, CNDO/2).[150,170]

The joint analysis of experimental data and results obtained by quantum-chemical methods will probably persist.

2. Electronic, photoelectron, and vibrational spectra

Communications concerning the application of UV spectroscopy as an analytical method in the study of protolytic equilibria, reactivities, and compositions of multicomponent mixtures of tetrazoles have occupied a leading position among publications of recent years. Thus UV spectroscopy has been used successfully to determine the acidity and basicity constants of 5-(*o*-, *m*-, and *p*-carboxyphenyl)tetrazoles in aqueous solutions of different acidity,[171] in the study of the rates and regioselectivities of the reactions of tetrazolate anions with dimethyl sulfate,[172,173] ethyl bromoacetate,[174] and methyl vinyl ketone,[175,176] and also in the study of equilibria involving ion pairs of the salts of 5-aryltetrazoles in acetonitrile.[174] Finally, bearing in mind the sensitivity of the UV spectra of the tetrazolate anions to the addition of small amounts of water, one may investigate quantitatively the specific solvation of tetrazolate ions in binary systems and also estimate the reactivities of specifically solvated tetrazole substrates.[173]

The luminescence spectra of 5-aryltetrazoles have been discussed.[177]

The photoelectron spectra (PES) of tetrazoles have their specific features and differ from those of other azoles, which is associated with the high ionisation potentials of tetrazoles by virtue of the enhanced stabilisation of the π levels.[178] According to photoelectron spectroscopic data, tetrazole exists in the gas phase almost exclusively as the 2*H*-tautomer.[148,179] A satisfactory agreement between spectroscopic data and the results of non-empirical calculations has been noted.[148,179] A publication[180] on the photoelectron spectra of certain condensed tetrazoles should be added to the studies quoted above.

Finally, we shall consider investigations of the vibrational spectra of tetrazoles. Thus the frequencies and the normal modes of vibration of 1-methyl- and 2-methyl-tetrazoles, 1-vinyl- and 5-vinyltetrazoles, 2-methyl-5-vinyltetrazole, and 5-phenyltetrazole have been analysed.[181,182] Detailed studies have been made of the vibrational spectra of the hydrazides of tetrazolylacetic acids[182] and tetrazole-containing polymers[183] and also of the IR and Raman spectra of 5-aminotetrazole.[184,185] Levchik et al.[185] interpreted the bands due to the stretching-deformation vibrations of 5-aminotetrazole (1000–1100 cm^{-1}) in terms of Fermi resonance. These data permit a reliable interpretation of the experimental spectra of tetrazoles, which extends the possibilities of vibrational spectroscopy as a method for the identification of compounds containing the tetrazole ring. Vibrational spectroscopy and ^{1}H and ^{13}C NMR spectroscopy can be used jointly in the analysis of tetrazoles having a complex structure. This approach has been demonstrated successfully in the analysis of polyvinyltetrazoles.[186]

3. NMR spectra

NMR spectroscopy has been used widely for the identification, structural study, and the prediction of the properties of tetrazoles. In a number of recent investigations the exceptional possibilities of ^{15}N NMR spectroscopy as a promising method for the investigation of polynitrogen heterocycles, and in particular tetrazoles, have been clearly demonstrated. This method proved extremely effective in the study of the prototropic tautomerism of tetrazole, since the chemical shifts of the ^{15}N nuclei of the pyrrole [N(1)] and pyridine [N(2)] atoms differ significantly.[187] According to Woffold et al.[187] and Bojarska-Olejnik et al.,[188] tetrazole in solution in DMSO-d_6 and $CDCl_3$ exists predominantly as the 1*H*-tautomer. The study of the ^{15}N NMR spectra of tetrazole and isomeric *N*-alkyltetrazoles led to the same conclusion.[189] It was shown that, for solutions of tetrazoles in DMSO or dioxane at concentrations not exceeding 0.5 M, it is possible to identify reliably the 1*H*- and 2*H*-tautomers and the isomeric *N*-alkyltetrazoles[166,189] and to demonstrate convincingly that 5-mercapto- and 5-hydroxy-tetrazoles exist mainly as the thiono- and oxo-derivatives respectively.[189] The structures of mono- and di-alkyl(alkenyl)tetrazoles,[190,191] complex condensed systems incorporating the tetrazole ring,[169] and also tetrazolium salts[191,192] have been established with the aid of ^{15}N NMR spectroscopy. The results of these investigations agree well with X-ray diffraction and gas electron diffraction data.[193] Interesting results have been obtained in a study[194] of tetrazoles by ^{15}N NMR spectroscopy. ^{15}N chemical shifts for a series of mono- and bicyclic tetrazoles and also for the salts and complexes of 5-substituted tetrazoles were determined. Together with the solution of the traditional problem — the determination of the individuality of the N(1)- and N(2)-isomers — ^{15}N chemical shifts were obtained for the tetrazolate anions taking into account data on the NH acidity of 5-substituted tetrazoles. A later study[190] dealt with the influence of the protonation of the tetrazole ring at the N(4) atoms on the ^{15}N chemical shift.

^{13}C NMR spectroscopy has also been used widely for the solution of structural problems in the chemistry of tetrazoles. The available information about the ^{13}C NMR spectra of isomeric *N*-substituted tetrazoles and other azoles has been surveyed and the data have been compared.[195] The torsional angles between the phenyl and azolyl fragments in *N*-aryltetrazoles have been estimated from ^{13}C NMR spectroscopic data,[196,197] and the electronic constants of the *N*(1)-tetrazolyl group have also been found.[196,198] ^{13}C NMR spectroscopy has been used in the study of 5-aryltetrazoles,[199] derivatives of 5-furyltetrazole,[200] and isomeric vinyltetrazoles[154,201,202] and also in the analysis of complex amino-imino equilibria involving 5-alkylamino-1-phenyltetrazoles.[203]

The most complete information about the structure of tetrazoles can be obtained by the joint application of ^{1}H, ^{15}N, and ^{13}C NMR spectroscopy. The tendency to carry out such studies is clearly manifested in recent publications.[154,168,169,191] It is noteworthy that the spin–spin coupling constants $J(^1H, ^1H)$,[204] $J(^{15}N, ^1H)$,[205] and $J(^{13}C, ^{13}C)$[206] as well as the nuclear Overhauser effect[207] are used together with the ^{1}H, ^{15}N, and ^{13}C NMR chemical shifts for the solution of structural problems, including the problem of the prototropic tautomerism and the identification of the isomeric *N*-alkyl(aryl)tetrazoles.

4. Thermolysis, combustion, and detonation

Tetrazoles possess extreme thermochemical characteristics among the azoles. The enthalpies of formation of tetrazole in the crystalline and gaseous states are ΔH_f(cr) = 236.1 kJ mol^{-1} and ΔH_f(g) = 327.2 kJ mol^{-1} respectively,[208,209] while the enthalpy of formation of crystalline 5-(tetrazol-5-yl)tetrazole is ΔH_f(cr) = 532.1 kJ mol^{-1}.[210] The standard enthalpies of combustion ΔH_c of tetrazole and 5-(tetrazol-5-yl)tetrazole are −916.1 and −1605.6 kJ mol^{-1} respectively.[208,210] The thermal decomposition of tetrazoles takes place in the temperature range 150–250 °C with dissociation of the N–N bonds.[211] According to the results of thermogravimetric analysis, the intense decomposition of tetrazoles is accompanied by an exothermic effect and a marked decrease in mass.[185] The thermal stability of tetrazoles is determined by the nature and location of the substituents in the heterocycle.[212–214] Thus an increase in the number of nitro-groups in nitroaryltetrazoles lowers their thermal stability.[214] The decomposition of the tetrazole ring is usually accompanied by the evolution of molecular nitrogen. However, the routes to the fragmentation of isomeric tetrazoles differ significantly. The thermolysis of 1,5-disubstituted tetrazoles leads to intermediate nitrenes,[215] while nitrile imines are formed from 2,5-disubstituted tetrazoles.[216,217] In all cases, the elimination of nitrogen proceeds via a highly polar transition state.[218] The rate-limiting stage of the thermal decomposition of 1,5- and 2,5-disubstituted tetrazoles is the homolytic dissociation of the N(1)–N(2) and N(2)–N(3) bonds respectively. The activation energies for these processes are in the range E_a = 162–200 kJ mol^{-1}. There is a linear relation between the logarithms of the rate constants for the thermal decomposition of tetrazoles and the Coulombic component of the perturbation energy (E_N). This makes it possible to predict the rate constants for the homolytic thermal decomposition of tetrazoles of different structure.[219] The characteristic features of the thermal decomposition of amino- and nitroamino-tetrazoles have been considered.[220,221]

It has been established that the rate-limiting stage in the thermolysis of poly-1-vinyltetrazole is the opening of the tetrazole ring. The activation energy for this process is 140–148 kJ mol^{-1}.[222] The thermal decomposition of the salts of 5-alkyl-2,3-diaryl- and 2,3,5-triaryl-tetrazolium salts has been discussed.[34,141]

In conclusion, it is essential to note that the fragmentation reactions of the tetrazole ring under the influence of a thermal pulse and electron impact have common features.[51] Joint examination of the thermal decomposition and mass spectra of tetrazoles yields valuable information about the nature of the reacting and intermediate species and about their reactivities.[223–227]

The characteristic features of the structure of the high-energy tetrazole ring predetermine the specific features of the combustion processes involving tetrazole and tetrazole-containing substances. These processes sometimes take place with unusual external effects, as happens in the combustion of mixtures of tetrazole and sodium tetrazolate.[50,228–230] A detailed study of the combustion of tetrazole has been carried out[231] and it has been shown that the process proceeds mainly in the condensed phase.

The characteristics of the transition of the combustion of the tetrazoles to detonation have been investigated in relation to the isomeric 1-methyl- and 2-methyl-5-nitrotetrazoles. Moulded 2-methyl-5-nitrotetrazole has much more effective detonation characteristics. The average time required for the transition from combustion to detonation is longer for 2-methyl-5-nitrotetrazole than for lead azide but shorter than for lead styphnate.[232] The capacity for detonation of complexes of 5-cyano-, 5-nitro-, and 5-nitroamino-tetrazoles as initiating explosives has been investigated experimentally.[233–235] Theoretical predictions of the detonation properties of tetrazoles have been made[236] and the methods for the analysis of the explosive properties of tetrazole derivatives have been discussed in a monograph.[237]

5. Acid–base properties

Tetrazole and 5-substituted tetrazoles are NH acids and weak organic bases, the acidity and basicity constants of which vary within wide limits depending on the nature of the substituent. Thus, on passing from 5-methyl to 5-nitro-tetrazole, the acidity constant increases while the basicity constant decreases approximately by seven orders of magnitude. The results of an experimental study of the acid-base properties of tetrazoles published up to 1990 have been surveyed in reviews[41,42] and in a monograph.[43] The same publications present tabulated acidity and basicity constants for a large number of tetrazoles. Among the studies in recent years, mention must be made of those in which the acidity and basicity have been investigated by various quantum-chemical methods and the proton affinities PA and PA^- of tetrazole and monosubstituted tetrazoles have been calculated.[160,168,238] The values of PA^- for the tetrazolate anion, calculated by the MNDO, AM1, and PM3 methods, are respectively 1567.5, 1351.3, and 1325.7 kJ mol^{-1}.[238]

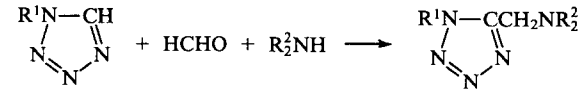
The calculations by Ostrovskii et al.[160] and Claramunt et al.[168] agree with the earlier experimental data for the basicity of tetrazoles. The protonation of tetrazoles of different structure at the nitrogen atom in the 4-position has been explained by the greater stability of the corresponding tetrazolium cation. It has also been shown[160] that there is a linear correlation between the calculated (MNDO) affinities PA and the experimental pK_{BH^+} for 5-substituted tetrazoles: pK_{BH^+} = 0.323PA − 49.01.

Unfortunately there have been as yet no experimental studies of the acidity and basicity of tetrazoles in the gas phase.

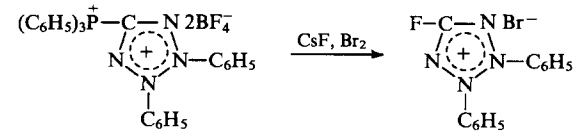
IV. Reactions of tetrazoles

1. Electrophilic substitution at a ring carbon atom

The reactions involving electrophilic substitution at a ring carbon atom in tetrazoles have been inadequately investigated. It has been shown recently that 1-alkyltetrazoles are smoothly iodinated by iodine in solution in sulfuric acid in the presence of potassium permanganate.[239] The corresponding 1-alkyl-5-iodotetrazoles are formed in 55%–75% yield. It has also been established that, when 1-methyltetrazole is treated with *tert*-butyllithium in tetrahydrofuran (THF), the hydrogen atom at a ring carbon atom in substituted by lithium.[240] The hydrogen at a ring carbon atom in 2,3-diaryltetrazolium salts is also substituted on treatment with *tert*-butyllithium in hexane.[241,242] 1-Substituted tetrazoles react with formaldehyde and amines under mild conditions, affording aminomethylation products.[59,243]

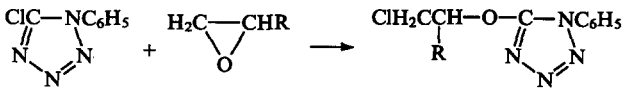


Finally, it is noteworthy that the triphenylphosphonium group in 2,3-diaryl-5-triphenylphosphoniotetrazolium is substituted by fluorine on treatment with caesium fluoride in the presence of bromine.[241]



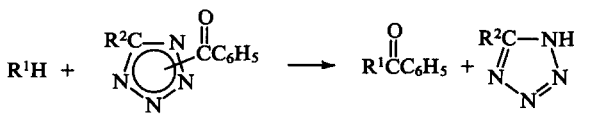
2. Nucleophilic substitution

The chlorine atom in 5-chloro-1-phenyltetrazole is readily substituted by treatment with alkali metal phenoxides in acetonitrile.[244] Similarly the chlorine atom in 5-chloro-1-phenyltetrazole is substituted by the SeH group on interaction of the tetrazole with sodium selenide in DMF at 100 °C.[245] Under phase transfer catalysis conditions, the corresponding ethers are formed in a satisfactory yield from 5-chloro-1-phenyltetrazole and various epoxy-compounds.[246]

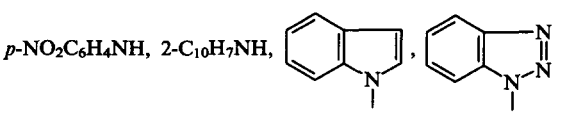


The bond between the sulfur and carbon atoms in 1-aryl-5-mercaptotetrazoles is cleaved on alkaline hydrolysis, which leads to the formation of 1-aryl-5-tetrazolols.[245]

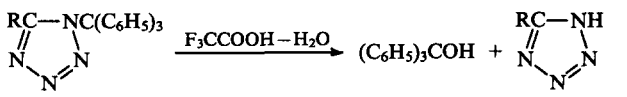
The tetrazole ring in 5-aryl-1-benzoyl- and 5-aryl-2-benzoyltetrazoles is readily substituted by various nucleophiles.[247] *N*-Benzoyltetrazoles are mild acylating agents, which are effective in reactions with primary and secondary aliphatic and aromatic amines as well as alcohols, benzimidazoles, and benzotriazole.



R^1 = C_2H_5O, C_6H_5O, *p*-$NO_2C_6H_4O$, 2-$C_{10}H_7O$, C_6H_5NH,



Compared with the widely used acylating agents *N*-benzoylimidazole and *N*-acylimidazoles,[248] 5-aryl-*N*-benzoyltetrazoles have significant advantages. The reactivity of *N*-benzoyltetrazoles is superior to that of *N*-acylimidazoles and these compounds also have a higher selectivity towards primary and secondary hydroxy- and amino-groups.[249] The use of *N*-benzoyl-tetrazoles is especially effective when the reactants and products are sensitive to acids and alkalis and are also thermally relatively unstable. The tetrazole ring in 1-triphenylmethyl-5-R-tetrazoles is readily substituted on treatment with trifluoroacetic acid in aqueous tetrahydrofuran.[78]

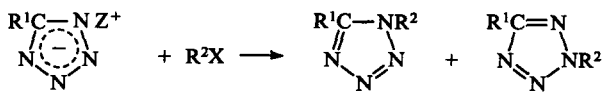


3. Alkylation

Alkylation belongs to the group of reactions of tetrazoles which have been investigated in greatest detail. It constitutes a simple method of synthesis of mono- and di-substituted tetrazoles of different structure, the preparation of which by other procedures is frequently impossible. Theoretically this reaction is of great interest, since it can serve as a convenient model for the study of heterocyclic substrates with dual reactivity.

Depending on the properties of the reaction medium, tetrazole, 5-substituted tetrazoles, as well as their salts enter into the alkylation reaction. Alkyl halides,[250-255] esters of sulfuric and aromatic sulfonic acids,[254] the acetates of nitroaminoalcohols,[256] and compounds containing activated double bonds [175,176,257,258] are used as the alkylating agents. Data on the application of alcohols, [259-262] unsaturated compounds (propene and isobutene),[263] certain nitrylium ions,[264] and vinyl ethers [265] for such purposes have been published recently. Separate mention should be made of the reactions of 5-substituted tetrazoles with aldehydes (formaldehyde) and amines, which result in the formation of *N*-aminomethyl(*N*-hydroxymethyl) derivatives of tetrazoles.[266-269]

It was postulated previously that, regardless of the nature of the alkylating agent and the properties of the reaction medium, the alkylation of tetrazole and 5-substituted tetrazoles always results in the formation of the corresponding 1- and 2-substituted tetrazoles.



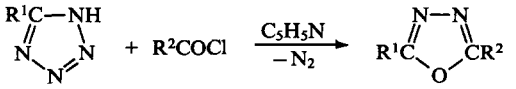
Z^+ = cation.

It was noted that the electronic nature of the substituents in the 5-position in the tetrazole ring exerts the main influence on the selectivity of this reaction—electron-donating and electron-accepting substituents promote respectively an increase and a decrease in the fraction of the *N*(1)-isomer in the alkylation products.[51] However, according to the latest data, exclusively 2-substituted tetrazoles are formed in the alkylation of tetrazole and 5-substituted tetrazoles by *tert*-butyl, isopropyl, or cyclohexyl alcohols in 96% sulfuric acid regardless of the nature of the substituent in the 5-position in the tetrazole ring.[262] Consequently, the selectivity of the alkylation of the tetrazoles depends also on the form (neutral or ionised) in which the substrate reacts with the alkylating agent. The high selectivity of the alkylation of the triethylammonium salts of 5-aryltetrazoles by methyl vinyl ketone in aprotic dipolar solvents [only the corresponding 4-(5-aryltetrazol-2-yl)butan-1-ones are formed] can be explained by the steric blocking of the N(1) atom of the tetrazole ring.[175,176]

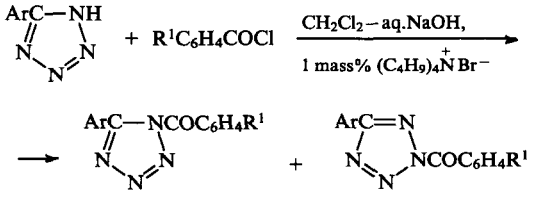
In the alkylation of tetrazoles under conditions of phase transfer catalysis and in homogeneous media, appreciable differences between the reaction selectivities were not discovered.[162] On the other hand, alkylation employing phase transfer catalysis is preparatively an extremely promising method, which makes it possible to obtain a wide variety of *N*-mono- and *N*,*N*′-disubstituted tetrazoles under mild conditions and in high yields using simple and readily available reagents and solvents.[270]

4. Acylation and imidoylation

Reactions of tetrazoles with acylating agents and imidoyl chlorides have recently acquired special importance, mainly because 2,5-disubstituted 1,3,4-oxadiazoles of different structure [142,247,270-273] as well as the previously unavailable 3*H*-1,3,4-benzotriazepines [274-277] can be obtained with their aid. Thus tetrazole and 5-substituted tetrazoles are converted into the corresponding 1,3,4-oxadiazoles in high yields on acylation by the chlorides of organic acids in the presence of organic bases at 100–120 °C.



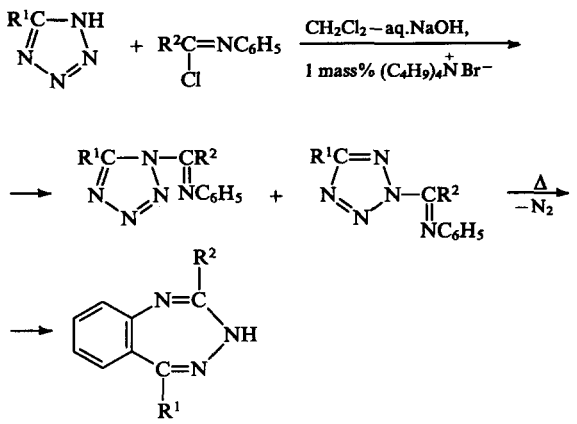
Previously it had been assumed that the first stage of this reaction involves the formation of an unstable 2-acyltetrazole, the cleavage of which with evolution of a nitrogen molecule leads to 1,3,4-oxadiazole.[278] However, subsequently it was demonstrated as a result of the application of phase transfer catalysis that the acylation of 5-aryltetrazoles by substituted benzoic acid chlorides affords not only 2-benzoyltetrazoles but also the isomeric 1-benzoyltetrazoles.[247,271]



The formation of oxadiazoles from 1-benzoyltetrazoles is preceded by isomerisation of the latter to 2-benzoyltetrazoles. It is suggested that, as a result of thermal cleavage and the elimination of a nitrogen molecule, 2-benzoyltetrazole is converted into an acylnitrile imine, the cyclisation of which leads to the oxadiazole.

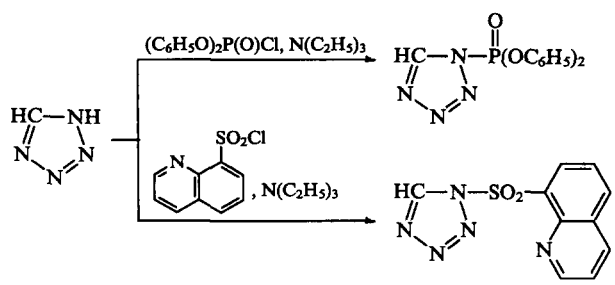
The results obtained in the study of the acylation of 5-substituted tetrazoles by carboxylic acid anhydrides are of greatest practical interest.[273] This reaction can be regarded as one of the most effective and simple methods of synthesis of 2(5)-mono- and 2,5-disubstituted 1,3,5-oxadiazoles.

During the last 30 years, it has come to be assumed that the reaction of 5-substituted tetrazoles with imidoyl chlorides, leading to 3,4,5-trisubstituted 1,2,4-triazoles, proceeds via a mechanism similar to that of the acylation reaction.[279] It was postulated that, on heating 5-substituted tetrazoles with imidoyl chlorides in pyridine, an unstable 2-imidoyl tetrazole is formed initially and is then converted into an imidoylnitrile imine as a result of thermal cleavage and elimination of a nitrogen molecule. The subsequent cyclisation of the imidoylnitrile imine leads to the 1,2,4-tetrazole. The study of this reaction under phase transfer catalysis conditions established that not only 2-imidoyltetrazole but also the isomeric 1-imidoyltetrazole is formed in the first stage. It is of fundamental importance that heating of the isomeric imidoyltetrazoles thus obtained in solutions in toluene, *m*-xylene, or dioxane and also in the absence of solvents results in the formation of the previously unknown 3*H*-1,3,4-benzotriazepines instead of the expected 3,4,5-trisubstituted 1,2,4-triazoles.[276,277]



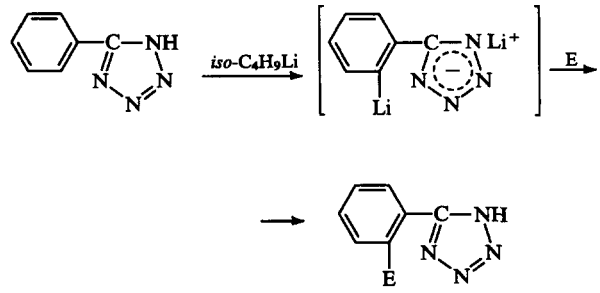
5. Silylation, phosphorylation, and sulfonylation

The interaction of the sodium salts of tetrazole with chlorotrimethylsilane results in the formation of trimethylsilyltetrazole in 85% yield.[47] The best solvent for this reaction is methylene chloride, while acetonitrile and DMF are virtually unsuitable. Begtrup and Larsen[47] do not discuss the problem of the selectivity of the silylation reaction, but one cannot rule out the possibility of the formation of two isomers — 1- and 2-trimethylsilyltetrazoles. It is surprising that the problem of regioselectivity has also not been discussed in the study of the phosphorylation[279] and sulfonation[280] of tetrazole. It is assumed that these reactions result in the formation of only 1-substituted tetrazoles.



6. Reactions of electrophiles with substituted tetrazoles

The reactions of 5-aryltetrazoles as well as 1-alkyl- and 2-alkyl-5-phenyltetrazoles with electrophiles of different nature have been investigated.[240,281–284] For example, it has been shown that, when 5-phenyltetrazole is treated with isobutyllithium in THF at −35 to −30 °C in the presence of tetramethylethylenediamine, the corresponding ionic intermediate is formed and reacts in situ with methyl iodide, acetaldehyde, or acrolein.[284]



It is striking that electrophilic substitution takes place only in the benzene ring and does not involve the tetrazole ring.

It is interesting that, when 5-alkyl-*N*-methyltetrazoles react under similar conditions, electrophilic substitution takes place in both *N*-methyl and *C*-alkyl groups.[285]

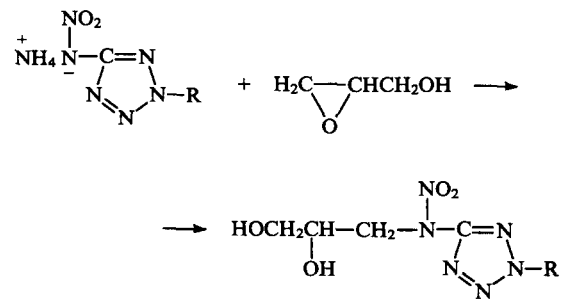
The nitration of 5-aminotetrazole and also of 1-alkyl- and 2-alkyl-5-aminotetrazoles by tetranitromethane in an alkaline medium leads to the corresponding 5-nitroaminotetrazoles.[286,287] Data exist on the nitration of condensed systems — 5,6-dihydro-7*H*-imidazolo[1,2-*d*]tetrazole, 7,8-dihydrotetrazolo-[1,5-*b*]1,2,4-triazine, and 5,6,7,8-tetrahydrotetrazolo-[1,5-*b*]-1,2,4-triazine[288] — as well as certain tetrazolium salts.[289]

Treatment of 5-aminotetrazoles with orthoesters results in the formation of the corresponding iminoesters,[290] whilst heating with nitriles in the presence of organoboranes affords amidines.[291] On treatment with thionyl chloride, 1-alkyl-5-aminotetrazoles are unexpectedly converted into 1,2,4-thiadiazoles.[292]

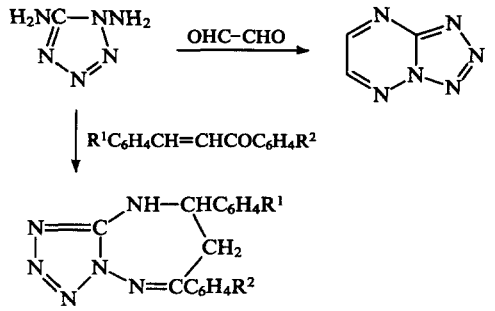


The acylation of 5-aminotetrazole at the amino-group by the chlorides of aromatic carboxylic acids[293,294] as well as the interaction of 5-aminotetrazole with *p*-cyanophenylcarbonylimidoyl chloride[295] have been described. In the latter case, the reaction also involves the exocyclic amino-group.

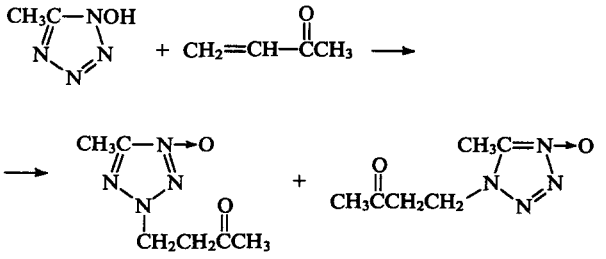
The salts of 2-alkyl-5-nitroaminotetrazole are alkylated by glycidol under mild conditions.[296] The tetrazole ring is not involved in this case.



1,5-Diaminotetrazole is an interesting reagent in the synthesis of heterocycles of various structures. Thus the interaction of 1,5-diaminotetrazole with glyoxal or unsaturated ketones leads to the formation of tetrazolo[1,5-*b*]-1,2,4-triazines and 5,7-disubstituted 5,6-dihydro-4*H*-tetrazolo[1,5-*b*]-1,2,4-triazepines respectively.[288,296]



When 1-hydroxy-5-phenyltetrazole is treated with epoxyalkanes, the reaction involves both the hydroxy-group and the tetrazole ring.[297] On the other hand, the reaction of 1-hydroxy-5-methyltetrazole with methyl vinyl ketone affords the corresponding isomeric *N*-oxides.[298]

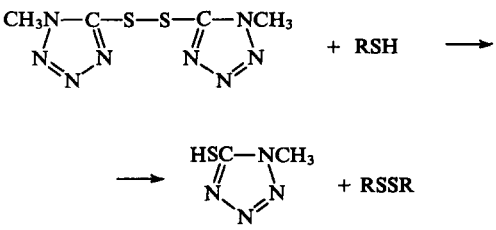


The tetrazole ring is not involved in the alkylation of bis(1-aryltetrazol-5-yl)methanes by methyl iodide,[299] in the arylation and alkylation of 1-phenyltetrazole-5-thiol by 1-chloro-2,4-dinitrobenzene[300] and *tert*-butyl isonitrile[301] respectively, and in the interaction of tetrazole-containing glyoximes with bromocyanogen.[302]

7. Reactions of nucleophiles with substituted tetrazoles

The interaction of tetrazole-5-diazonium chloride with substituted anilines affords a high yield of 3-aryl-1-(tetrazol-5-yl)triazepines.[302] Treatment of 1-alkyl- and 2-alkyl-5-chloroethyltetrazoles with an alcoholic solution of sodium hydroxide led to the formation of the corresponding 5-vinyltetrazoles.[303]

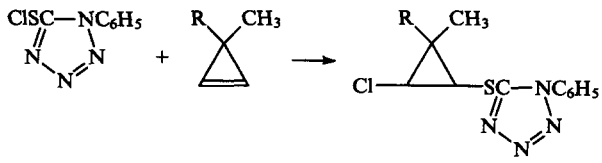
The reactions of 1-alkyl(aryl)tetrazole-5-thiols with nucleophiles (thiols, alcohols) have attracted continuous attention. This is because they can be used to synthesise substances with biological activity.[304] Thus it has been observed that bis(1-methyltetrazol-5-yl) disulfide exhibits an exceptionally high reactivity in relation to thiols.[305-307]



This reaction[306] is a convenient method of synthesis of both symmetrical and asymmetric disulfides.

S-Heteroaryl derivatives of 1-phenyltetrazole-5-thiols are also readily cleaved by potassium hydroxide in the water–acetonitrile system.[245]

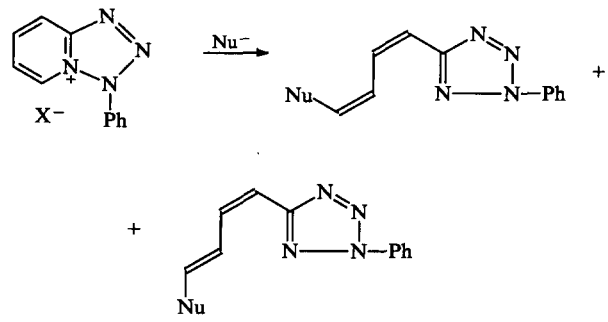
3,3-Disubstituted cyclopropenes interact with 1-phenyltetrazole-5-sulfenyl chloride in solution in methylene chloride at −20 °C.[308]



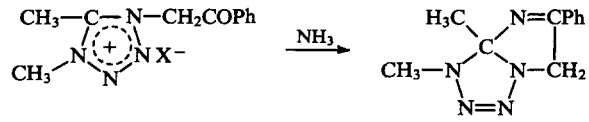
On treatment with unsaturated alcohols in the presence of tertiary amines, *S*,*S*′-bis(1-phenyltetrazol-5-yl) dithiocarbonate is hydrolysed under mild conditions.[309,310]

Grignard reagents may be used to obtain a series of tetrazole derivatives with functional group substituents.[311-313]

Finally, it is noteworthy that treatment of tetrazolylpyridinium salts with nucleophiles entails the dissociation of the N–C bond in the six-membered heterocycle.[314]

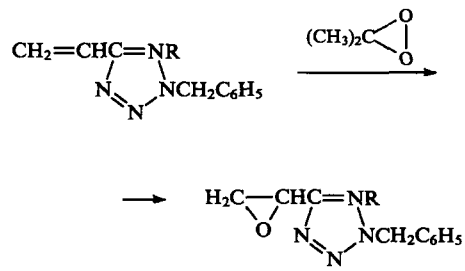


On the other hand, 2,3-dimethyl-4-benzoylmethyltetrazolium salts are converted into dihydro-3*H*-imidazo[1,2-*d*]-tetrazoles on treatment with ammonia.[315]

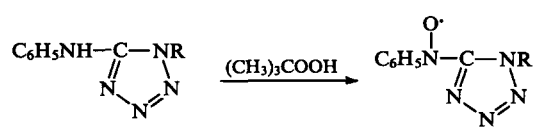


8. The effect of oxidants and reductants

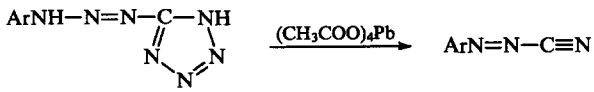
The tetrazole ring is resistant to the action of oxidants. The nature of the reactions between tetrazoles and oxidants depends on the nature and position of the substituent in the heterocycle. Thus interaction of 2-benzyl-5-vinyltetrazole with dimethyldioxirane results in the formation of the corresponding epoxide.[316]



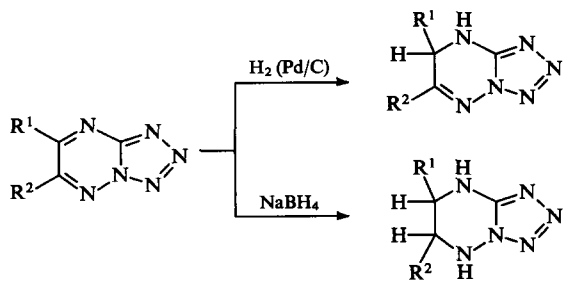
while the oxidation of 5-arylaminotetrazoles by *tert*-butyl peroxide afforded stable nitroxyl radicals.[317]



On the other hand, treatment of 1-aryl-3-(tetrazol-5-yl)triazenes with lead tetraacetate results in the degradation of the heterocycle.[318]



The ring is usually not involved in the reactions with reductants. It has been shown[288] that the reduction of tetrazolo-[1,5-*b*]-1,2,4-triazines by hydrogen (Pd/C) entails only partial hydrogenation of the six-membered ring, whereas in the reduction by sodium tetrahydroborate in methanol the corresponding 5,6,7,8-tetrahydrotetrazolo[1,5-*b*]-1,2,4-triazines are formed in a high yield.

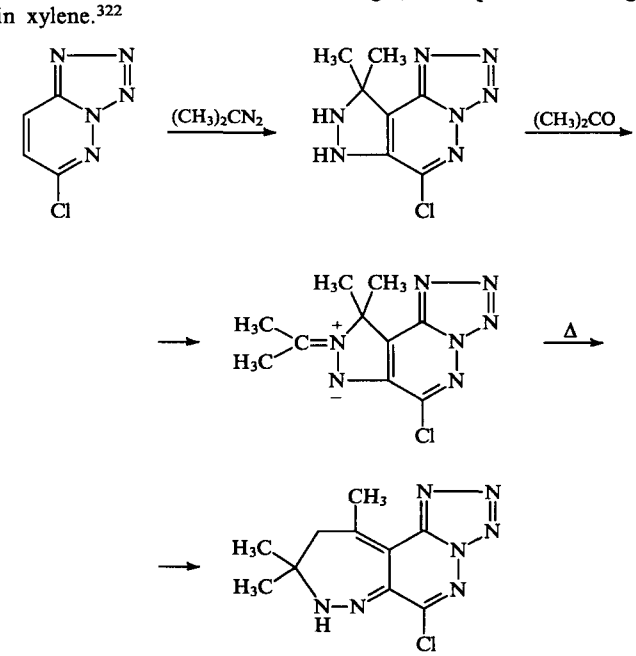


Satisfactory results have been obtained in the catalytic (Pd) reduction of 5-(2-naphthoxy)-1-phenyltetrazole by tetrabutylammonium hypophosphite in the benzene–water two-phase system.[319]

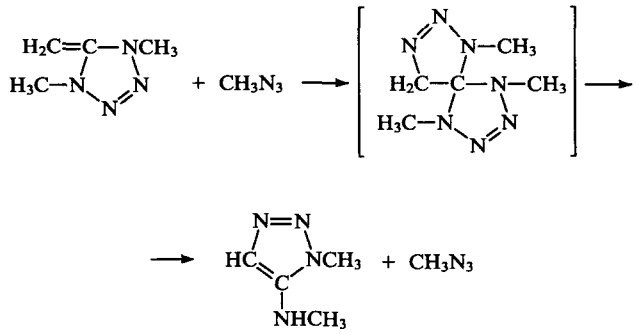
A small number of studies on the electrochemical reduction of tetrazoles have been published in recent years. It has been found that the electrochemical reduction of 1-vinyl- and 5-vinyltetrazoles in acetonitrile proceeds with the transfer of one electron.[320] The electrochemical reduction of 5-trichloromethyltetrazole leads to the formation of tetrazole and 5-chloromethyl- and 5-dichloromethyl-tetrazoles in 16%, 5%, and 28% yields respectively.[53]

9. Cycloaddition reaction

In connection with the active search for methods of synthesis of new heterocyclic systems, there has been an appreciable growth of interest in cycloaddition reactions with participation of tetrazoles as dipolarophiles.[321] It has been shown that the interaction of 6-chlorotetrazolo[1,5-*b*]pyridazine with diazoalkanes results in the formation of the corresponding cyclic adducts. The interaction of the latter with acetone leads to stable azomethine imines, which are converted into tetrazole-containing 1,2-diazepines on heating in xylene.[322]



On treatment with methyl azide, 4,5-dihydro-1,4-dimethyl-5-methylenetetrazole isomerises to 1-methyl-5-methylamino-1,2,3-triazole.[140] It is believed[140] that an unstable cyclic adduct is formed in the first stage of this reaction and then decomposes to the corresponding triazole and methyl azide.



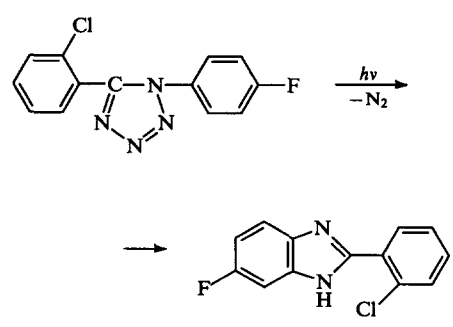
The formation of a stable cyclic adduct can be detected in the reaction of phenyl azide with 4,5-dihydro-1-methyl-5-(1-methylethylidene)-4-phenyltetrazole in cyclohexane.

10. Polymerisation of vinyltetrazoles

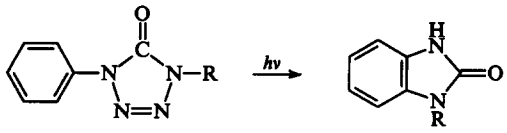
Vinyltetrazoles polymerise fairly readily in solution or in bulk in the presence of radical catalysts, for example azobisisobutyronitrile. Important data for the understanding of the mechanism of the polymerisation of vinyltetrazoles and for the prediction of the polymers formed have been obtained in a study of the polymerisation of 1-vinyl-, 5-methyl-1-vinyl-, and 2-methyl-5-vinyltetrazoles in aqueous solutions of sodium thiocyanate.[323] It was shown that the polymerisation of these compounds is in many respects similar to the polymerisation of acrylonitrile under similar conditions and is apparently of a complex-radical type. The use of sodium thiocyanate solutions as the reaction medium makes it possible to obtain tetrazole-containing polymers with a high molecular mass and the polymerisation process is much faster than in organic solvents. Together with the homopolymerisation, a study was made of the copolymerisation of 1-vinyl- and 2-methyl-5-vinyltetrazoles with acrylic and methacrylic acids, their derivatives, and styrene.[324–326] It was established that very long blocks of homopolymer units may be formed in the copolymer macrochain in the copolymerisation of 2-methyl-5-vinyltetrazole with acrylonitrile, which indicates a tendency by vinyltetrazole to undergo homopolymerisation. On the other hand, the probability of the formation of copolymer blocks is higher in the copolymerisation of 2-methyl-5-methylenetetrazole with methacrylic acid and its esters.

11. Photochemical reactions

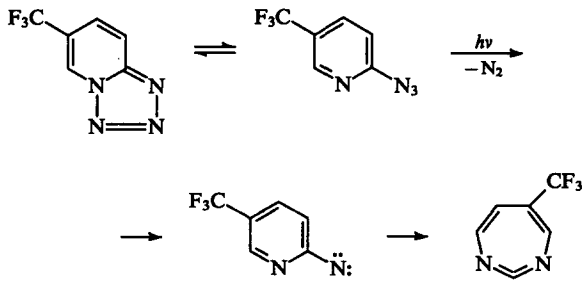
The photolysis of tetrazoles entails their fragmentation with liberation of a nitrogen molecule and the formation of a new heterocyclic system. Thus satisfactory yields of the corresponding benzimidazoles can be obtained from 1,5-diaryltetrazoles.[327]



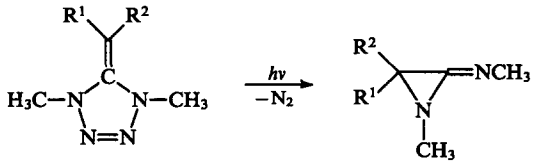
1,4-Disubstituted 4,5-dihydrotetrazol-5-ones undergo similar reactions.[328-330]



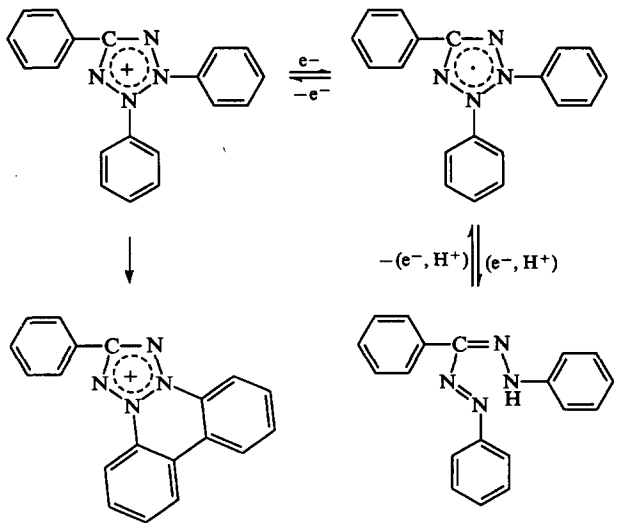
Interesting results have been obtained in a study of the photolysis of tetrazolopyridines containing the trifluoromethyl group in the six-membered ring.[331] This reaction can be regarded as a method of synthesis of 1,2-didehydro-1,3-diazepines, which are difficult to obtain.



The mechanism of the photolysis of 2,5-disubstituted tetrazoles has been investigated.[332] It has been shown that the corresponding nitrile imines are intermediates in these reactions. The formation of iminoaziridines has been detected in the photolysis of 5-alkylidene-4,5-dihydrotetrazoles.[333]



The mechanism of the photochemical reduction of 2,3,5-triphenyltetrazolium chloride has been investigated in aqueous solutions at pH 9–11.5 by the method of flash photolysis. A mechanism involving the formation of an intermediate tetrazolium radical has been proposed for this reaction.[334]



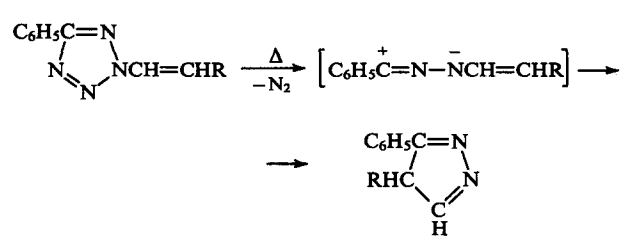
12. Metal complexes of tetrazoles

Systematic studies on the structures and properties of metal complexes of tetrazoles and also the capacity for complex formation of the corresponding heterocyclic ligands were not initiated until the beginning of the 1980s.[335-338] The unsubstituted tetrazole readily forms complexes with cobalt(II), nickel(II), copper(II), and cadmium(II) chlorides.[335] It has also been shown that 1- and 2-monoalkyltetrazoles interact with copper(II) chloride and thiocyanate, affording crystalline complexes. Regardless of the reactant ratio and the nature of the tetrazole ligand (T), complexes having the general formula CuT_2X_2 are formed.[339,340] Tetrazoles substituted in the 1- and 2-positions are monodentate ligands which are coordinated to the central copper atom via one of the nitrogen atoms. It is significant that 1-alkyltetrazoles show a greater tendency to form complexes than the 2-isomers.[336] The cobalt(II) and cobalt(III) complexes of 5-substituted tetrazoles have been investigated in detail.[341-343] It has been shown that the interaction of 5-aminotetrazole with pentamminecobalt nitrate results in the formation of the complex $[Co(NH_3)_5T](NO_3)_3$.[343] The indium(III) and iron(III) complexes PMT, where P is the octaethylporphyrin dianion and M the corresponding metal ion, have been obtained by the reaction of azidoporphyrins with nitriles.[344,345] Numerous complexes of 1,5-disubstituted tetrazoles with cobalt(II), nickel(II), copper(II), and iron(III) chlorides have been obtained. It has been shown that the crystalline complexes $CuTCl_2$ are formed in a high yield in the interaction of 1,5-disubstituted tetrazoles with $CuCl_2$ in organic solvents at 25–30 °C.[340] The molecules of the 1,5-disubstituted tetrazoles apparently serve as bridging ligands in such complexes. Each molecule of the tetrazole ligand is bound simultaneously to two neighbouring Cu^{2+} ions linked to one another by Cl^- bridging ions. Barium complexes of 1,5-disubstituted tetrazoles have been described.[346] 1,5-Disubstituted 4,5-dihydrotetrazoles proved to be effective siderophores.[347,348] When the methyl esters of 2-(1-R-4,5-dihydrotetrazol-5-yl-alphaidene)cyanoacetic esters are treated with iron(III) chloride ether, blue cryptocrystalline complexes FeT_3 are formed. Each of the three molecules of the tetrazole ligand in such complexes is coordinated to the central Fe^{3+} ion via a nitrogen atom of the heterocycle and the carbonyl oxygen atom. When iron(III) chloride is replaced by $FeSO_4$, the polymeric complex $(FeT_2)_n$ is produced.

The complexes of 2,5-disubstituted tetrazoles have been investigated to a much lesser extent. The complexes of 2-methyl-5-vinyltetrazoles with chromium(III), nickel(II), cobalt(II), and palladium(II) chlorides have been recently described. It has been shown that the metal ion in such complexes is coordinated to the N(4) atom of the tetrazole ligand.[349,350] The mercury(II) and palladium(II) complexes of tetrazolium salts have been described.[351,352]

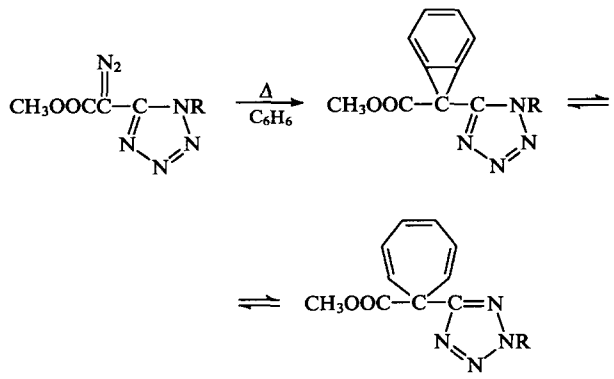
13. Other reactions

In this section, it is necessary to mention primarily the conversion of 2-alkenyl-5-phenyltetrazoles into the corresponding 4-alkenyl-3-phenylpyrazoles.[282] The alkenyltetrazoles are fragmented on heating in 1,2-dichlorobenzene, the yield of pyrazoles being 79%–98%.

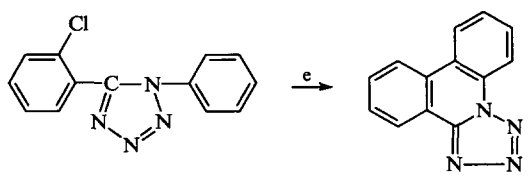


This reaction can be regarded as a method of synthesis for 3,4-disubstituted pyrazoles which are difficult to obtain.

The isomeric *N*-substituted 5-(methoxycarbonyldiazomethyl)tetrazoles undergo interesting reactions on heating.[353] The different influences of the isomeric tetrazolyl substituents on the functional groups in the side chain can be clearly traced in this example.



The electrochemical cyclisation of 5-(*o*-chlorophenyl)-1-phenyltetrazole to tetrazolo[1,5-*a*]phenanthridine has been investigated.[354]



Finally, it has been shown recently that trichloroacetonitrile adds smoothly to 1-methyl- and 2-methyl-5-vinyltetrazoles,[355,356] that 4,6-dinitrotetrazolo[1,5-*a*]pyridine forms stable adducts with alkoxide anions,[357] and that the acid hydrolysis of 5-diazomethylazotetrazole results in the formation of 5-hydrazinotetrazole.[358]

V. Applications of tetrazoles

There has been a steady growth of publications devoted to the applications of tetrazoles during the last decade. A systematic analysis of this problem, involving the examination of 700 patents published in 20 countries, has been carried out.[359] It follows from this analysis that the main applications of tetrazoles are in medicine, biochemistry, agriculture, analytical chemistry, information recording systems, and energy consuming processes as corrosion inhibitors and energy consuming materials. The most significant results have been obtained in the synthesis of tetrazole-containing β-lactam antibiotics of the cephalosporin series.[1,3,360,361] Such antibiotics exhibit a high antimicrobial activity, a prolonged action, and a low toxicity. Highly effective antiviral preparations have been found among tetrazoles.[362] 3-Tetrazole analogues of azidothymidine (AZT) have been obtained recently. It has been predicted that they should be active against the AIDS virus.[118] *C*-Glycosyltetrazoles—potential inhibitors of *E. coli* dehydrokinase-synthetase—have been described.[68] Preparations possessing antitubercular activity have been widely investigated.[4,6,8] Studies devoted to the creation of tetrazole-containing antihypertensive (losartan) and antiangina preparations, which belong to the new generation of regulators of cardiovascular activity, merit special attention.[7,11] Certain tetrazolium salts exhibit a high radioprotecting activity. The use of these compounds ensures the survival of up to 60% of animals irradiated with a lethal dose.[363]

Tetrazole is a condensing agent in the synthesis of oligonucleotides and also in systems for the automated synthesis of polynucleotides. In a number of instances, it is superior to other nitrogen-containing heterocycles used for these purposes.[16,17,364,365] Date have been published recently concerning the preparation of new generation herbicides on the basis of tetrazole-containing compounds.[20] Tetrazolium salts are widely used in analytical chemistry as extractants for the lanthanide metals[366] and in information recording systems, including their use as components of low-silver photographic materials.[21,25] 5-Mercapto-1-phenyltetrazole is a DIR component in modern photoprogramming systems and is one of the best antifogging agents.[22] Finally, highly effective corrosion inhibitors,[367] components of pyrotechnic and gas-generating compositions, and explosives[368,369] have been found among tetrazoles.

VI. Conclusion

Little more than a hundred years have elapsed since the discovery of tetrazoles. Interest in these compounds was aroused at the beginning of the 1950s when the principal methods of synthesis of tetrazoles were developed and studies on their physicochemical properties were initiated. Some diminution of interest in tetrazoles towards the end of the 1960s was rapidly replaced by its rearousal, and active studies on the chemistry of these compounds have been continued to the present.

Tetrazoles are exceptionally important in synthetic chemistry. They are used in the syntheses of many nitrogen-containing heterocycles—pyrazoles, imidazoles, 1,2,4-triazoles, 1,3,4-oxadiazoles, and what is especially important, the previously unavailable 3*H*-1,3,4-benzotriazepines.

Unfortunately no new advances have been made recently in the development of new general methods of synthesis of tetrazoles. This problem still awaits solution.

There have been considerable achievements in the practical application of tetrazoles, especially in medicine and biochemistry. An increase in the production of tetrazoles in industrially developed countries has been noted.

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