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REARRANGEMENTS AND TRANSFORMATIONS OF 1,2,3-THIADIAZOLES IN ORGANIC SYNTHESIS. (REVIEW)

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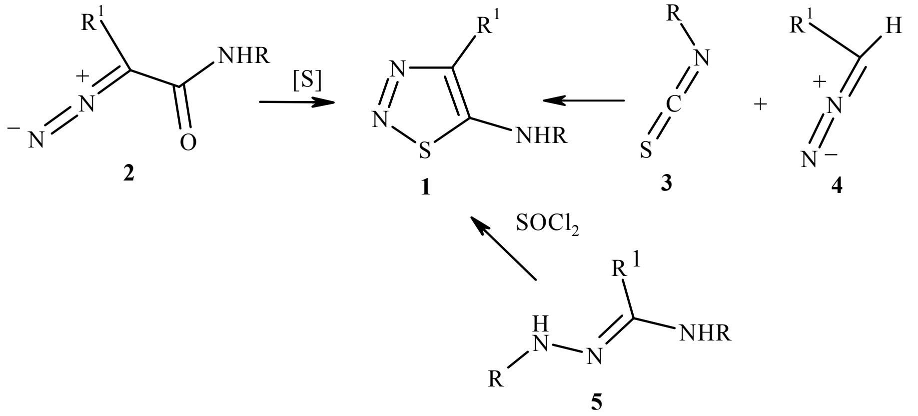
Published information and the results of the authors' investigations on the use of the rearrangements and transformations of 1,2,3-thiadiazole derivatives in organic synthesis is reviewed.

Keywords: nitrogen-containing heterocycles, alkynethiolates, acetylenes, diazo compounds, sulfur-containing heterocycles, rearrangements, thioketenes.

1,2,3-Thiadiazoles **1** can be obtained easily by one of three methods: 1) Thionation of α-diazocarbonyl compounds **2** (the Wolff method [1-7]); 2) cycloaddition of isothiocyanates **3** to diazo compounds **4** (the Pechmann method [8-11]; 3) reaction of the hydrazones of α-methylene ketones **5** with thionyl chloride (the Hurd–Mori reaction [12-15]).



According to data from *Chemical Abstracts*, about 2000 scientific papers and patents on the synthesis and study of 1,2,3-thiadiazole derivatives have been published in the last 20 years. The constantly growing interest in this type of compound is due primarily to the biological activity of the derivatives of this heterocycle. The 1,2,3-thiadiazole ring is a component of such preparations as *Dropp* (*Thidiazuron*) the defoliant of the fine-fibered cotton plant [16], the cephalosporin antibiotic *Cephuzonam* [17], and the product *Bione* that stimulates the immune system of plants [18]. At the same time 1,2,3-thiadiazoles are widely used as synthons in organic synthesis.

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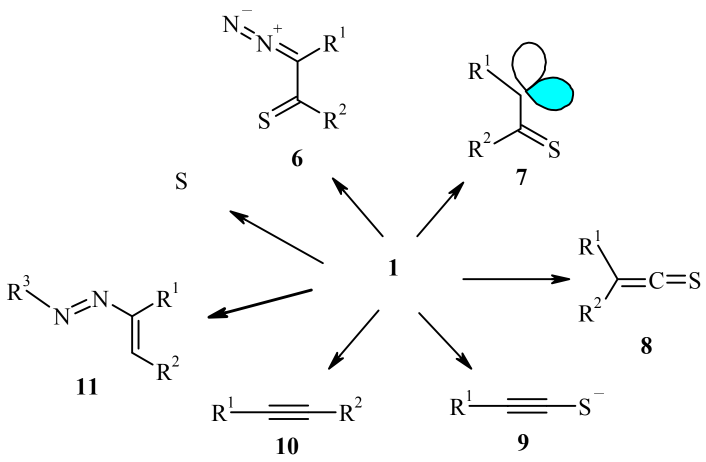
Several reviews have recently been devoted to the chemistry of 1,2,3-thiadiazoles [20-25]. Their synthesis, structure, and properties have been described in detail. Two reviews [22, 24], published in 1990 and 1996, include data on the rearrangements of 1,2,3-thiadiazoles. However, the transformations were not considered as a method of synthesis. In the present review data on the use of the transformations and rearrangements of 1,2,3-thiadiazoles in organic synthesis are examined and analyzed.

1. INTERMEDIATES IN THE REARRANGEMENTS AND TRANSFORMATIONS OF 1,2,3-THIADIAZOLES

The wide variety of chemical transformations in the 1,2,3-thiadiazole ring is largely due to the fact that they readily form various highly reactive compounds.

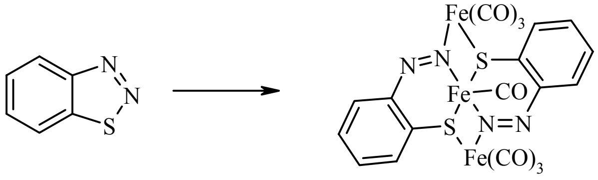


Cleavage of the N–S bond leads to opening of the ring with the formation of the α-diazothione **6**, containing two reaction groups (thione and diazo). Loss of a molecule of nitrogen leads to the α-thioxocarbene **7**, which can rearrange to another highly reactive compound – the thioketene **8**. Treatment of 1,2,3-thiadiazole with a base (R^2 = H, Cl) leads to the formation of the alkynethiolate **9**. The simultaneous loss of molecules of nitrogen and sulfur by the action of radiation or heat leads to the alkynes **10**. During heat treatment the formation of 1,2-diazo-1,3-butadiene **11** is possible.

1.1. α-Diazothiones

$$\mathbf{1} \rightleftharpoons \mathbf{6} \rightleftharpoons \text{Cyclization}$$

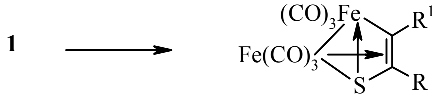
The α-diazothiones **6** have been postulated as intermediates in the rearrangements of 1,2,3-thiadiazoles to other heterocyclic systems [22]. However, it was only possible to isolate them in the form of complexes with $Fe_2(CO)_9$. When the 1,2,3-benzothiadiazole **12** was held with $Fe_2(CO)_9$ in hexane, the complex **13** was obtained [26]. The structure of **13** was confirmed by X-ray crystallographic analysis. Analogous complexes were isolated for aliphatic α-diazothiones [27].



12 **13**

1.2. Thioxocarbenes. Biradicals

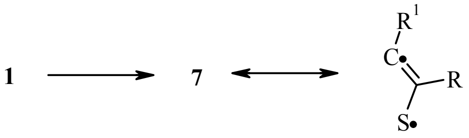
During thermal or photochemical decomposition of 2,4-disubstituted 1,2,3-thiadiazoles **1** the carbenes **7**, containing a thioketone group at the α-position, are formed [28-32]. These carbenes were characterized in the form of the complexes **14**.



$R = R^1 = Ph$, $(CH_2)_n$ ($n = 4, 6$)

14

The structure of the α-thioxocarbene **7** suggests π conjugation between of the carbene orbital and the π-electrons of the thione function. In a number of papers [33-35] the carbenes **7**, formed during the decomposition of 1,2,3-thiadiazoles, were assigned the structure of biradicals.



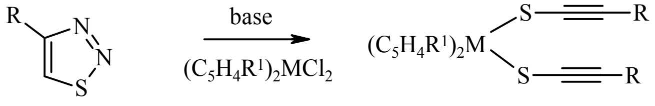
This intermediate is characterized by both intramolecular and intermolecular reactions, taking place by a radical or carbene mechanism.

1.3. Thioketenes

The formation of thioketenes **8** is possible during thermal decomposition (pyrolysis or flash thermolysis) of 1,2,3-thiadiazoles **1** [36-44]. The transformation involves the following processes: Elimination of nitrogen from the ring; 1,2-shift of the substituent R^1. The structure of the thioketenes was confirmed by means of the NMR spectra using D and ^{13}C isotopic tags [37, 41] and also by microwave [40, 45] and IR spectra with Fourier transformation [42].

1.4. Alkynethiolates

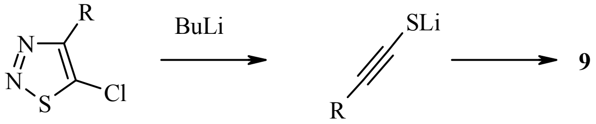
The alkynethiolates **9** can be generated by the action of strong bases or radiation on 4-monosubstituted 1,2,3-thiadiazoles **15** [46-49]. In [50] complexes of alkynethiolates **16** with metallocenes were obtained.



15 **16**

M = Ti, Ni, Sm

The alkynethiolates **9** were also obtained during the treatment of 5-chloro-1,2,3-thiadiazoles **17** with Grignard reagents or organolithium compounds [51].



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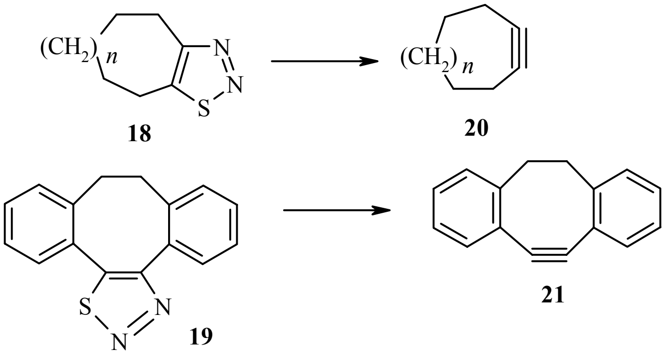
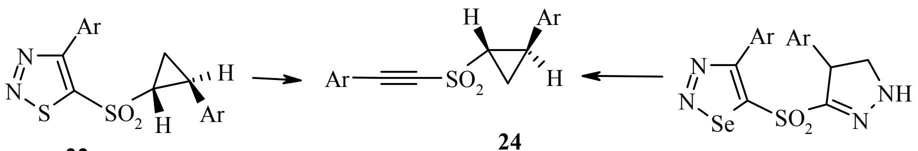
1.5. Acetylenes

It was shown that the alkynes **20** and **21** respectively are formed during the decomposition of 1,2,3-thiadiazoles **18** and **19** (with the simultaneous loss of a nitrogen molecule and a sulfur atom) [52, 53].



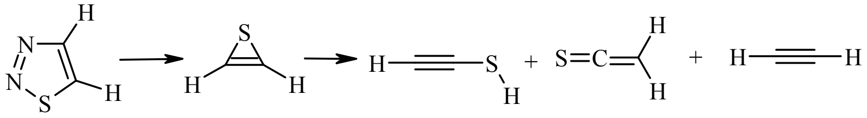
18 **20** **21** **19**

The arylethynyl sulfones **24** were synthesized by the pyrolysis of 1,2,3-thiadiazole **22** and 1,2,3-selenadiazole **23** [54].



22 **24** **23**

It should be noted that the alkynethiol **26**, the thioketene **27**, and acetylene were detected during study of the thermal decomposition of unsubstituted 1,2,3-thiadiazole **25** [47].



25 **28** **26** **27**

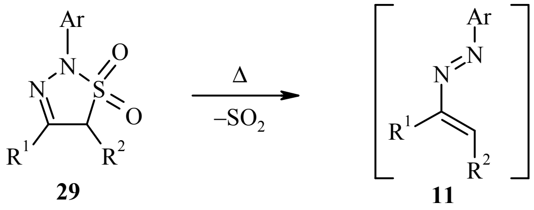
Data from calculations of the relative stability of such structures by empirical methods and by *ab initio* methods were presented in [38, 39, 42]. It was shown that thioketene **27** was 74 kJ/mol more stable than ethynethiol **26** and 552 kJ/mol more stable than thiirene **28** [38].

1.6. Sulfur

Not only the nitrogen but also the sulfur can be eliminated during the decomposition of 1,2,3-thiadiazoles **1**. The sulfur in turn can also enter into reaction with compounds present in the reaction mass [55]. Thus, 1,2,3-thiadiazoles can act as thionating reagents.

1.7. 1,2-Diaza-1,3-butadiene

Highly reactive diazabutadienes **11**, which readily enter into cycloaddition, are formed during the thermal decomposition of 2-aryl-1,1-dioxo-1,2,3-thiadiazolines **29** (70-110°C) [56].

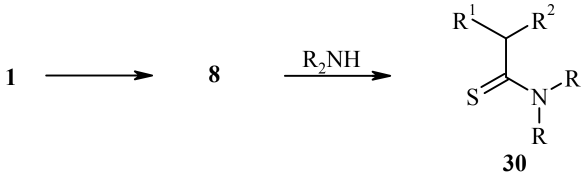


2. SYNTHESIS OF ORGANIC COMPOUNDS USING REARRANGEMENTS AND TRANSFORMATIONS OF 1,2,3-THIADIAZOLES

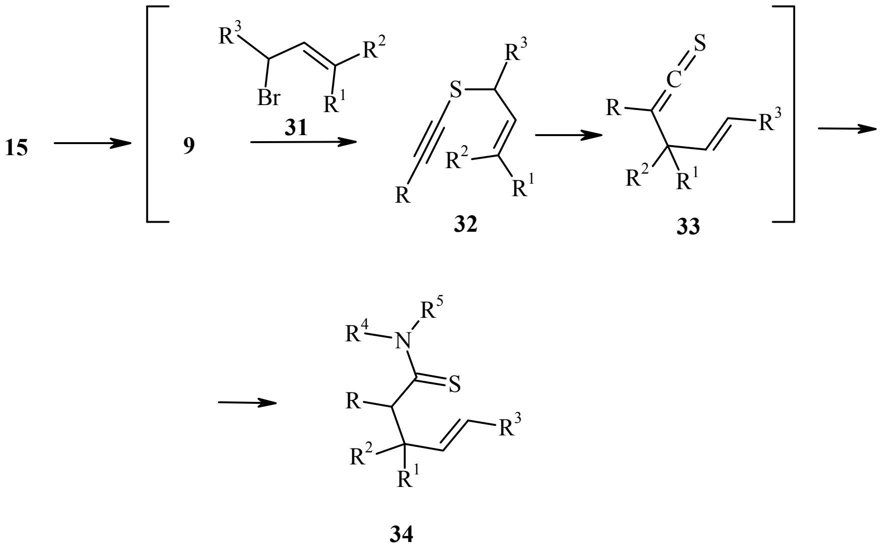
The highly reactive particles generated by cleavage of the 1,2,3-thiadiazole ring are widely used in organic synthesis. Examples of organic compounds that can be obtained by transformation of the 1,2,3-thiadiazole ring are presented below.

2.1. Acyclic Compounds

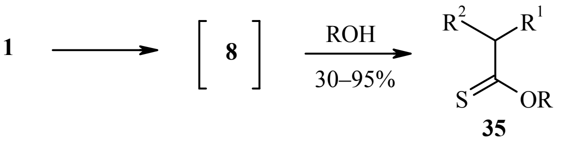
The photochemical decomposition of 1,2,3-thiadiazoles **1** in the presence of amines leads to the formation of thioamides **30** [36, 57, 58] with yields of 60-75%.



An original method for the synthesis of thioamides by the transformation of derivatives of the 1,2,3-thiadiazole ring was described in [48]. The ethynethiolates **9** generated by treatment of 1,2,3-thiadiazoles **15** with butyllithium were alkylated with the bromoallyl derivatives **31**. The obtained compounds **32** underwent rearrangement to the thioketenes **33**, which in reaction with amines gave the thioamides **34**, containing a double bond at the γ-position.

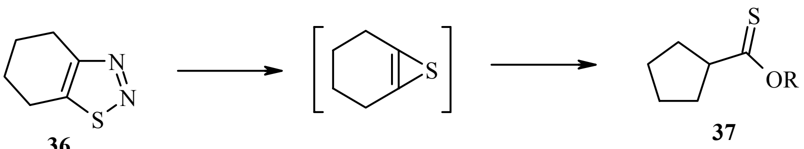


During the thermolysis of photolysis of 1,2,3-thiadiazoles **1** in alcohol the thioesters **35** were obtained [59-62].



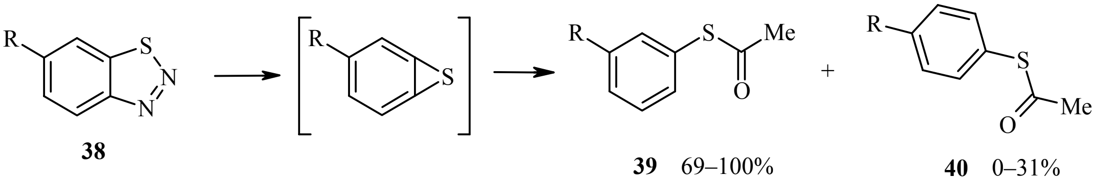
R^1, R^2 = Me, Et, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2OH$

In [59, 61] it was shown that thermal or photochemical decomposition of 4,5,6,7-tetrahydro-1,2,3-thiadiazole **36** in solutions of glycols (ethylene glycol or diglycol) led to the formation of the cyclopentanethiocarboxylic ester **37**, i.e., the reaction was accompanied by contraction of the cyclohexene ring to cyclopentane.

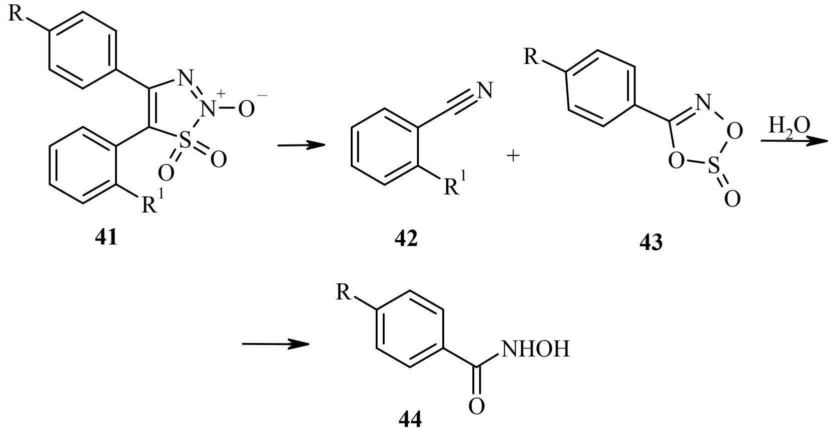


R = CH_2CH_2OH, $(CH_2)_2O(CH_2)_2OH$

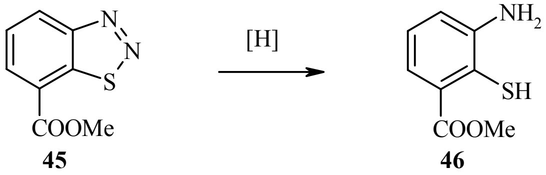
Thioesters of acetic acid were obtained during acylation of the products from decomposition of the benzothiadiazoles **38**. It was shown that the reaction took place with the formation of two isomeric thioesters **39** and **40** [63].



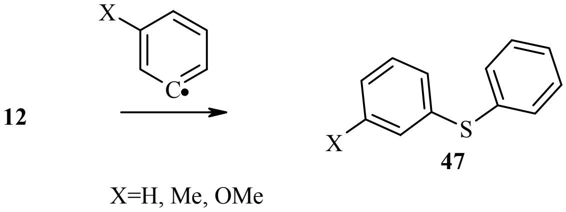
The nitriles **42** and 1,3,2,4-dioxathiazole 1-oxides **43** were synthesized by the decomposition of 1,2,3-thiadiazole 1,1,2-trioxides **41**. Hydrolysis of the products gave the hydroxamic acids **44** with yields of 38-85% [64-66].



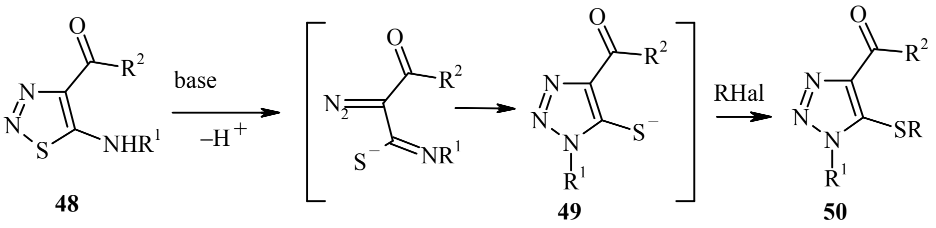
It was shown that reduction of the benzothiadiazole **45** with hydrogen on palladium gives methyl 3-amino-2-mercaptobenzoate **46** [67].



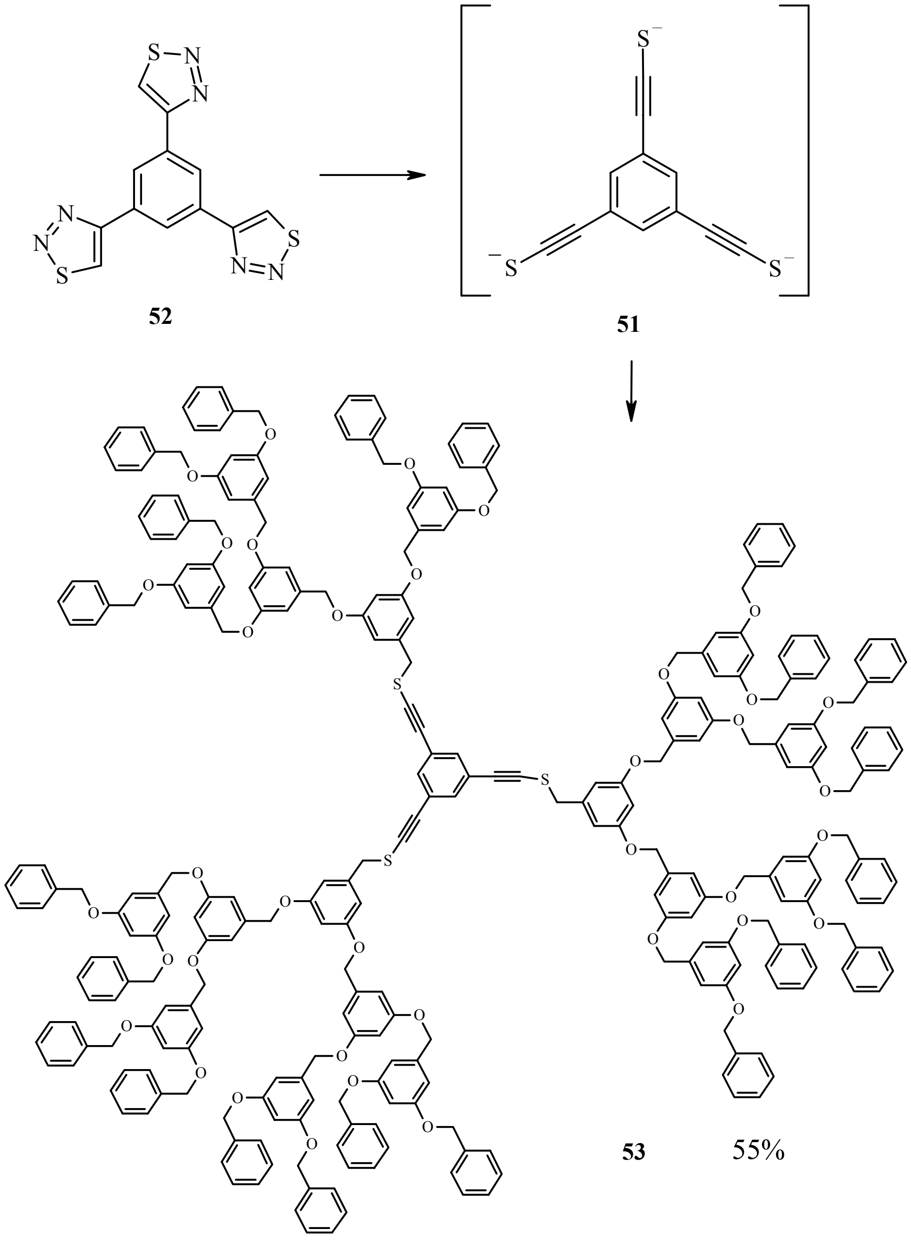
Decomposition of the benzothiadiazole **12**, which takes place by a radical mechanism, often leads to the formation of the sulfides **47** [68-72].



A synthesis of sulfides, where the key stage is a Dimroth rearrangement of the 1,2,3-thiadiazole ring, was described in [73-75]; the transformation of 5-amino-1,2,3-thiadiazoles **48** to 5-sulfanyl-1,2,3-triazoles **49** followed by reaction with alkyl (hetaryl) halides with the formation of 1,2,3-triazolyl sulfides **50** gives yields of 80-98%.



The decomposition of the 1,2,3-thiadiazole ring by the action of bases with the formation of alkynethiolates was used for the synthesis of various dendrimers [24]. The Frechet dendrimer **53** was obtained by the reaction of the tristhiolate **51**, generated from tristhiadiazolylbenzene **52**, with benzyl bromide [76].

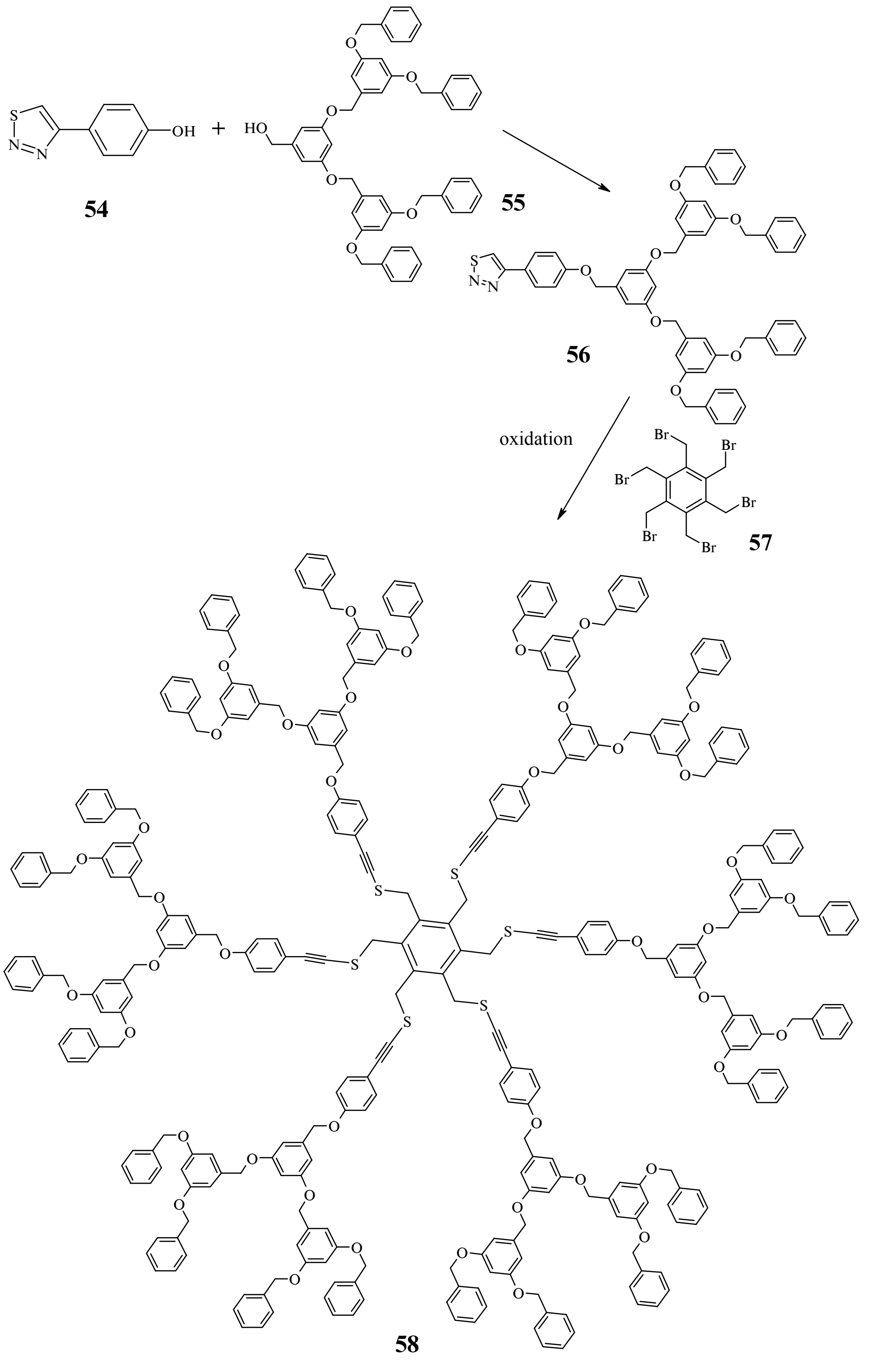


52

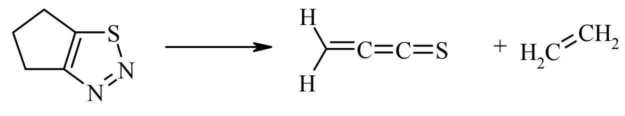
51

53 55%

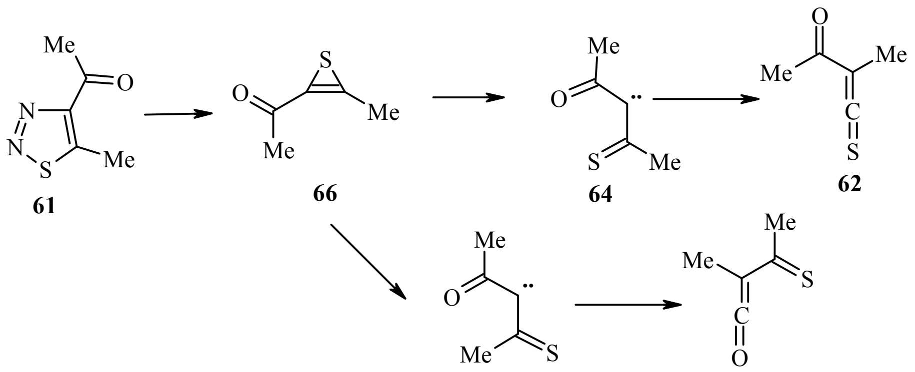
Another example of the synthesis of dendrimers based on the transformation of 1,2,3-thiadiazoles is the insertion of the Frechet dendron residue into the 1,2,3-thiadiazole ring followed by decomposition of the thiadiazole ring and alkylation of the obtained thiolate. Thus, the ether **56** was obtained by the Mitsunobu reaction of 4-(4-hydroxyphenyl)-1,2,3-thiadiazole **54** with the benzyl alcohol derivative **55** [77]. Compound **56** was converted by treatment with a base into a dendrone alkynethiolate, which was converted by reaction with hexa(bromomethyl)benzene **57** into the dendrimer **58**.



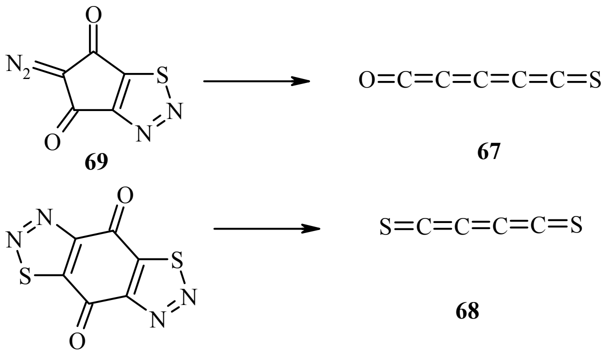
Decomposition of the 1,2,3-thiadiazole ring was also used for the generation of such highly reactive intermediates as heterocumulenes. The propadienethione **60** and ethylene were produced by the photolysis of cyclopenteno-1,2,3-thiadiazole **59** [78, 79].


59 **60**

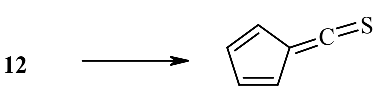
During study of the thermal decomposition of 4-acetyl-5-methyl-1,2,3-thiadiazole **61** it was shown [31] that the intermediates in the production of the thioketene **62** and the ketene **63** are the *s-cis-s-cis* and *s-trans-s-cis* stereoisomers of the obtained carbene **64** and **65** respectively. The isomerization is explained by the existence of the cyclic thiirene structure **66**.


61 **66** **64** **62** **65** **63**

The heterocumulenes **67** and **68** were obtained by photolysis of the thiadiazole **69** and the bisthiadiazole **70** [80, 81].


69 **67** **70** **68**

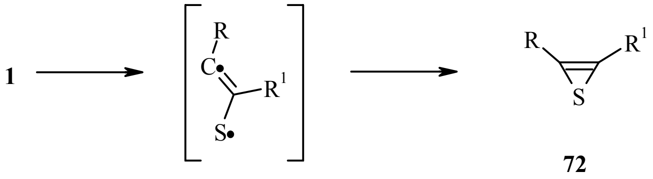
During thermolysis the benzothiadiazole **12** forms the thioketene **71** [39].


71

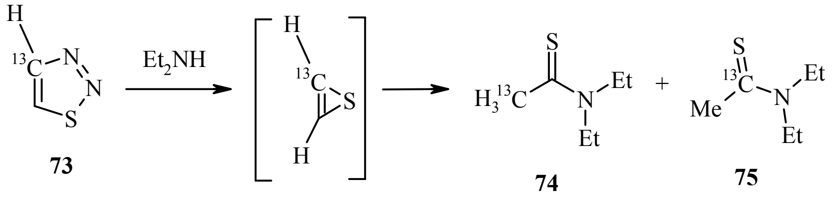
The transformations of 1,2,3-thiadiazoles are used more widely in the synthesis of various heterocyclic systems than for the production of linear structures. In the next section we give examples of the synthesis of heterocycles using the transformations and rearrangements of 1,2,3-thiadiazole derivatives.

2.2. The Synthesis of Three- and Four-Membered Heterocycles

The formation of the antiaromatic thiirene ring **72** from 1,2,3-thiadiazole **1** has long been the subject of debate and detailed study [29, 31, 37, 41, 57, 82-91].

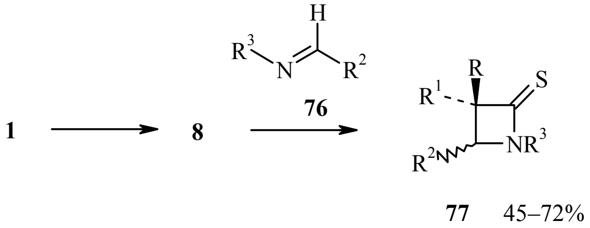


1,2,3-Thiadiazoles containing D [37] and ^{13}C [83] at positions 4 and 5 were synthesized in order to obtain evidence for the formation of the thiirene **72**. In all cases an equal distribution of the isotopes was found in the products from transformation of the 1,2,3-thiadiazole. For example, the photodecomposition of 4-^{13}C-1,2,3-thiadiazole **73** in the presence of diethylamine led to a uniform distribution of the ^{13}C isotope in the thioamides **74** and **75** [58]. These facts favor the existence of an intermediate cyclic thiirene structure.

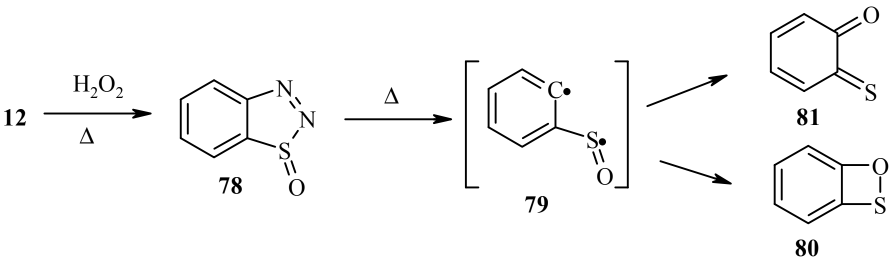


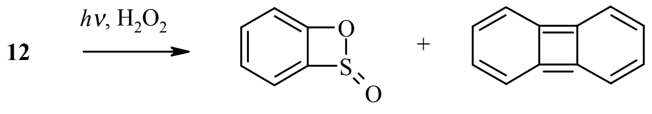
More recently [85] the thiirene **72** was identified at 8-20 K by IR spectroscopy. It was shown [86] that electron-accepting substituents stabilize this 4π-electron antiaromatic heterocycle.

A convenient method for the synthesis of the β-thiolactam ring is the cycloaddition of thioketenes to azomethines. Thus, the stereoisomeric derivatives of β-thiolactams **77** can be obtained by cycloaddition of the thioketenes **8**, produced by the decomposition of 1,2,3-thiadiazoles **1**, to the azomethines **76** [92].



During the thermal decomposition of 1-oxo-1,2,3-benzothiadiazole **78** benzoxathiete **80** or its valence tautomer **81** is formed [35]. Photochemical oxidation of the benzothiadiazole **12** leads to the formation of benzoxathiete S-oxide **82** and biphenylene **83** [35].

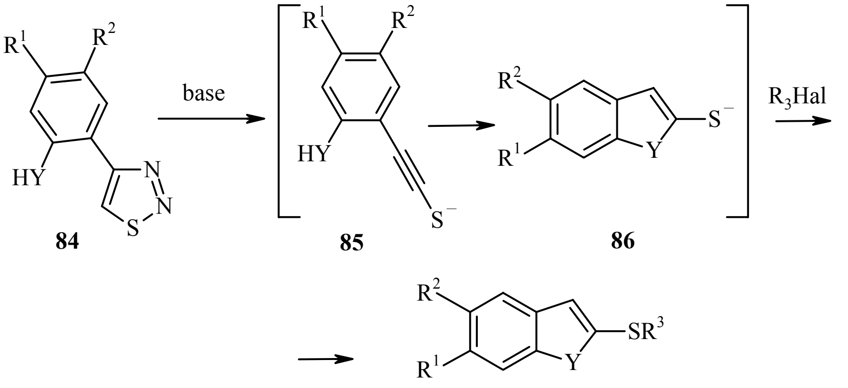




82 25% **83** 45%

2.3. The Synthesis of Five-membered Heterocycles

The transformations of 1,2,3-thiadiazoles **84** were used for the synthesis of benzofurans. 2-(*o*-Hydroxyphenyl)alkynethiolates **85**, formed during the decomposition of 4-(*o*-hydroxyphenyl)-1,2,3-thiadiazoles **84** by the action of bases, undergo cyclization to 2-benzofuranthiolates **86**, the alkylation of which leads to 2-benzofuranyl sulfides **87** [93-95]. 2-Methylthioindoles were obtained similarly from 4-*o*-aminophenyl-1,2,3-thiadiazoles [93].

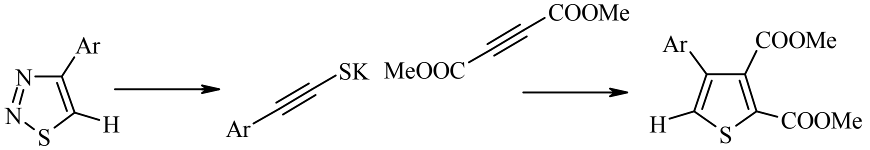


84 **85** **86**

87 70–92%

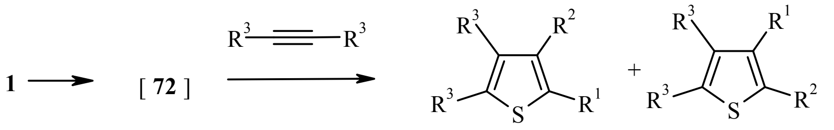
Y= O, NR

The thiophenes **88** were obtained [96] by the reaction of dimethylacetylenedicarboxylate with potassium arylethynethiolate **89**, synthesized from 5-aryl-1,2,3-thiadiazole **90**.



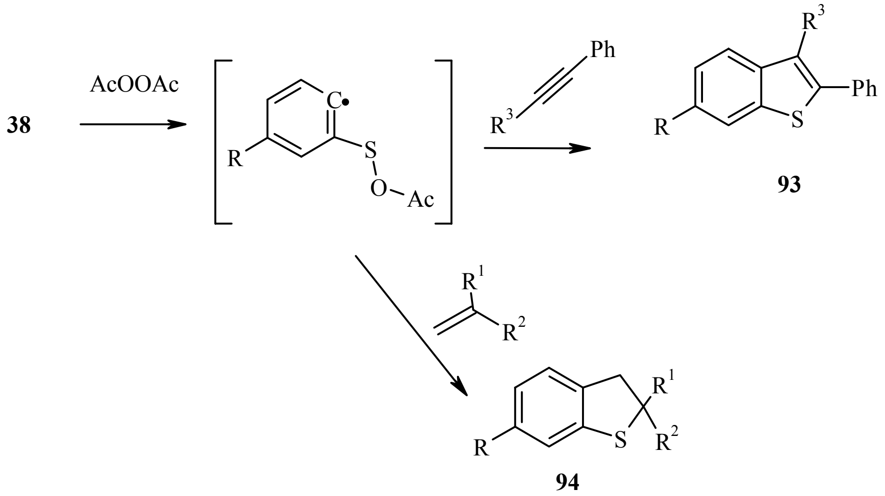
90 **89** **88** 70–90%

The thiirene **72**, produced during the thermal decomposition of 1,2,3-thiadiazole **1**, reacts with acetylenes with the formation of a mixture of two isomeric thiophenes **91** and **92** in a ratio of 1:1 [30, 33, 97, 98].

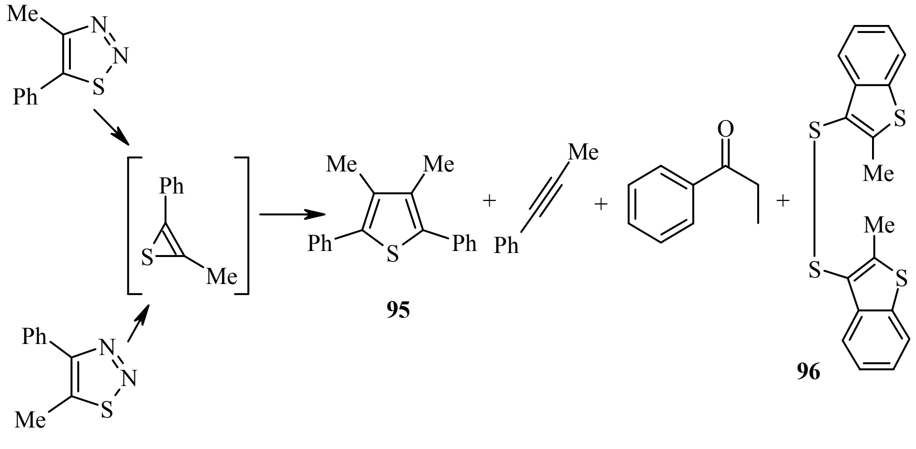


91 **92** 52–76%

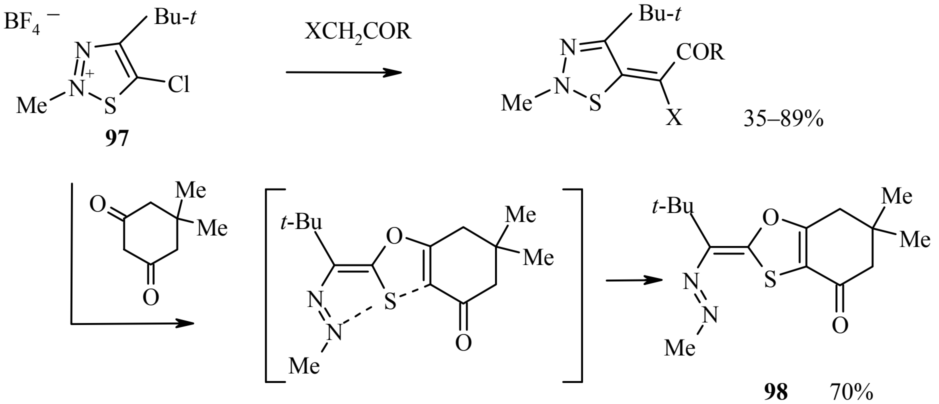
At the same time, during the transformation of the benzothiadiazoles **38** in the presence of acetylene with various substituents only one of the isomeric benzothiophenes **93** is formed [97]. However, this example only applies to thermal decomposition catalyzed by peroxides. The reaction with alkenes takes place similarly with the formation of the thiophene **94**.



1,2,3-Thiadiazole can serve as source of both thioketene and acetylene. Thus, thiophenes are formed during the decomposition of 1,2,3-thiadiazoles under the influence of various factors (radicals, temperature, radiation) [33, 61, 68, 69, 71, 72, 99, 100]. However, the reaction is less regioselective (e.g., [55]). During the decomposition of 4-methyl-5-phenyl-1,2,3-thiadiazole and its isomer 5-methyl-4-phenyl-1,2,3-thiadiazole side products (phenylpropyne, its hydrolysis product phenyl ethyl ketone) and also the disulfide of 2-methylbenzothiophene **96** are often formed in addition to the thiophenes **95**.



L'Abbe [101] found that in the reaction of the 5-chloro-2-methyl-1,2,3-thiadiazolium salt **97** with dimedone nucleophilic substitution of the chlorine atom at position 5 of the thiadiazole ring takes place not with the methylene carbon atom in dimedone, as in [102], but with the keto oxygen atom. It is followed by opening of the thiadiazole ring and cyclization at the thione function with the formation of the oxathiole **98**.

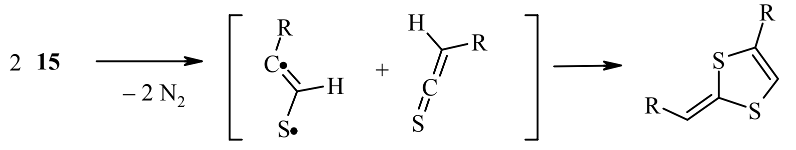


97

35–89%

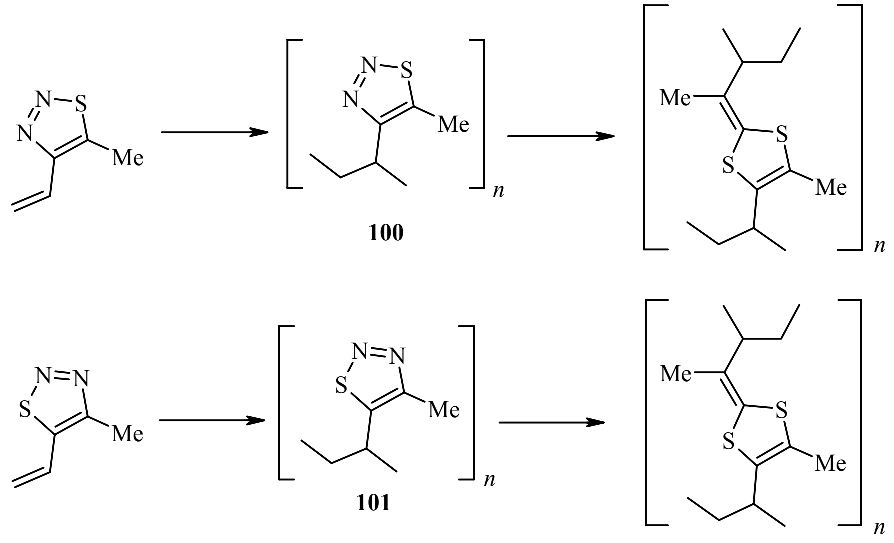
98 70%

The formation of 1,3-dithioles is typical of thermal or photochemical decomposition of the thiadiazole ring [33, 61, 62, 89, 103-109]. Thus, the 1,2,3-thiadiazoles **15** are converted during thermolysis or base catalysis into the dithioles **99** with yields of up to 90% [33, 61, 89, 103-106, 110-114]. The final structure contains fragments of two molecules of the initial thiadiazole.



99

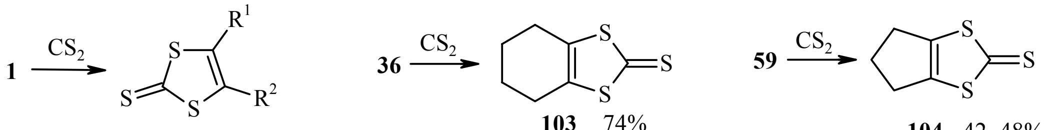
This approach to the synthesis of 1,3-dithioles was also used for the synthesis of photopolymers. Linear polymers that can undergo cross-condensation under the influence of light of a specific wavelength were obtained on the basis of vinyl-1,2,3-thiadiazoles [115, 116]. It was shown that irradiation of the poly[1,2,3-thiadiazol-4(5)-yl]vinyls **100** and **101** led to decomposition of the 1,2,3-thiadiazole rings and intermolecular cyclization to dithiole rings, resulting in cross linking of the adjacent polymers.



100

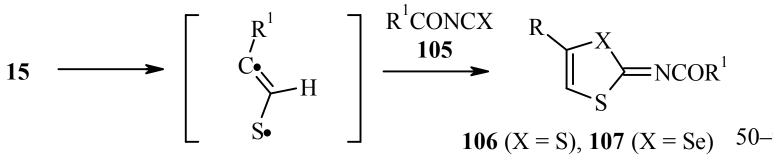
101

The dithiole-2-thiones **102-104** can be synthesized by the decomposition of 1,2,3-thiadiazoles **1**, **36**, and **39** in the presence of carbon disulfide [117-120].



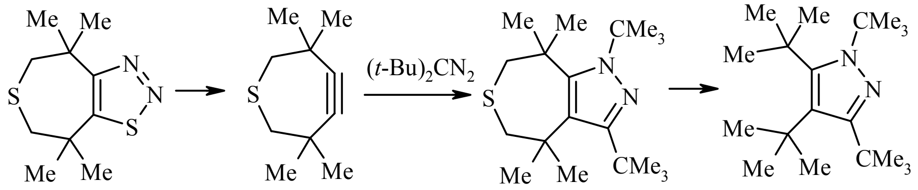
102 74% **103** 74% **104** 42–48%

If the decomposition of 1,2,3-thiadiazoles **15** is conducted in the presence of the isothiocyanates **105**, the 2-iminodithioles **106** are formed. Isoselenocyanates can also be used in this transformation, leading to the formation of 2-iminothiaselenoles **107** [121-123].



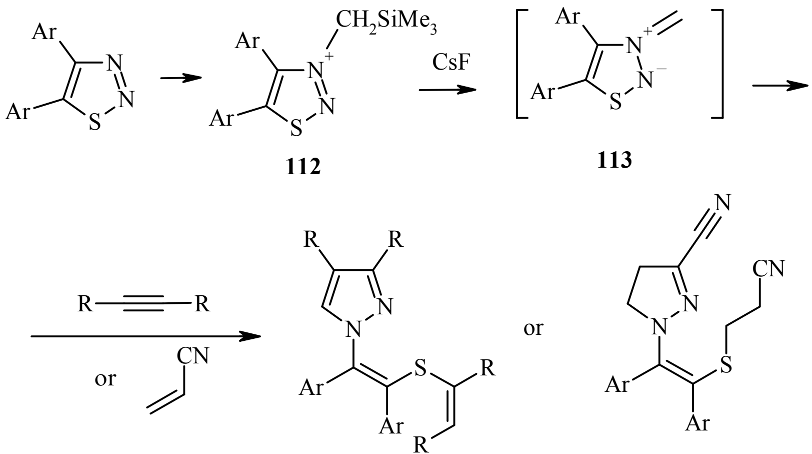
106 (X = S), **107** (X = Se) 50–96%

Tetra-*tert*-butylpyrazole **111** was synthesized by the reaction of di-*tert*-butyldiazomethane and the cyclic alkyne **109**, obtained by transformation of the 1,2,3-thiadiazole **108**. The reaction takes place through the intermediate **110**, which is converted into the final product **111** as a result of reductive desulfurization [124].



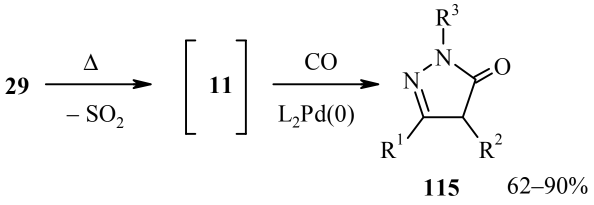
108 **109** **110** **111** 30%

It was also found that when treated with CsF the 3-substituted thiadiazole **112** forms the dipole **113**, which is converted in reaction with alkynes and alkenes into the pyrazoles **114** [125].

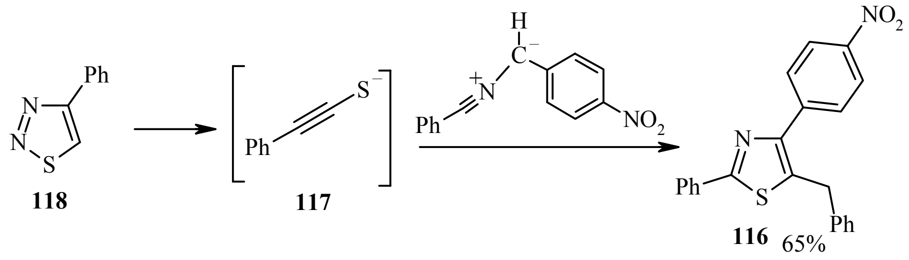


112 **113** **114** 85–92%

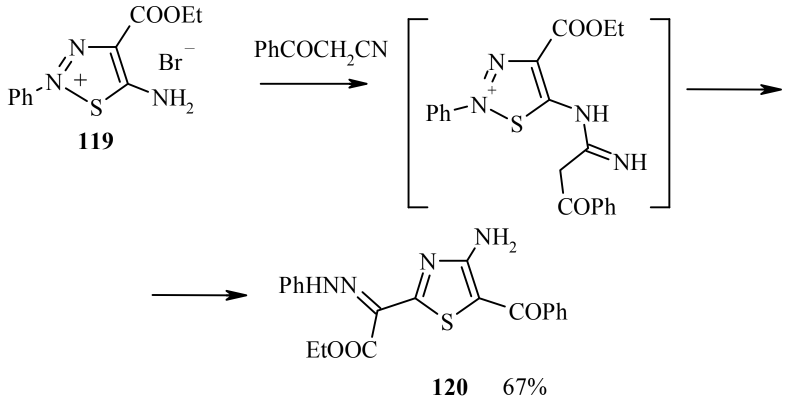
1,2-Diaza-1,3-butadiene **11**, generated during thermal decomposition of the thiadiazoline **29**, enters readily into a cheletropic reaction with CO [126] with the formation of 2,3-pyrazol-1(5H)-one **115**.

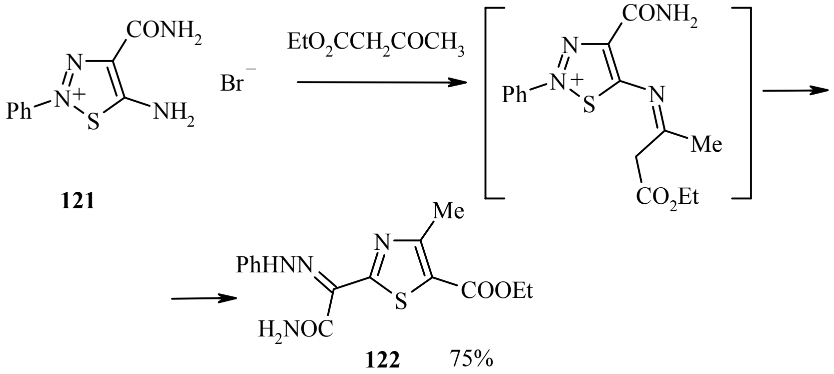


The thiazole **116** was obtained by the cycloaddition of 1-phenyl-3-(*p*-nitrophenyl)nitrile ylide with 2-phenylethynethiolate **117**, generated from the 1,2,3-thiadiazole **118** [127].

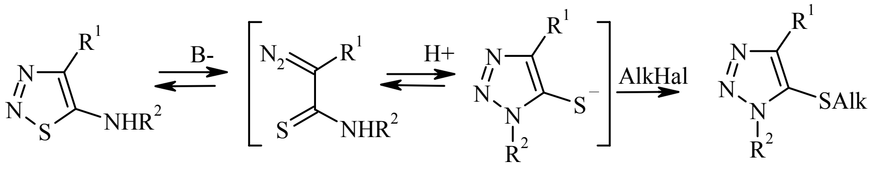


The 4-amino-5-benzoylthiazole **120** was obtained by the transformation of the 2-phenyl-1,2,3-thiadiazolinium salt **119** by the action of benzoylacetonitrile [128]. It was also shown that 5-ethoxycarbonyl-4-methylthiazole **122** is formed as a result of reaction of the salt **121** with acetoacetic ester.





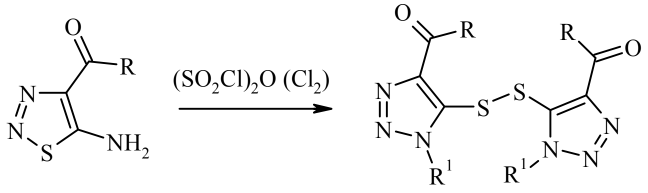
All the published examples of rearrangements of 1,2,3-thiadiazoles to 1,2,3-triazoles can be divided into two groups. In the first it is possible to include the most widely published Dimroth rearrangement [11, 74, 129-134]. Under the influence of bases such as sodium hydroxide, sodium carbonate, triethylamine, and aliphatic amines 5-amino-1,2,3-thiadiazoles rearrange to 5-sulfanyl-1,2,3-triazoles. The transformation is reversible. The reverse rearrangement takes place in an acidic medium. Alkylation of the sulfur atom is usually employed to detect the 1,2,3-triazole structure [132, 133]. The obtained alkylthio derivatives **123** are not able to undergo the reverse rearrangement.



123 80–97%

R^1 = H, Alk, Ar, CO_2Alk, COAr; R^2 = H, Alk, Ar

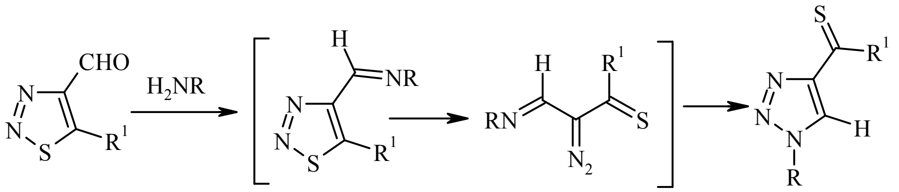
In [135] we discovered an anomalous case of the Dimroth rearrangement of 1,2,3-thiadiazoles in an acidic medium. It was shown that the esters and amides of 5-amino-1,2,3-thiadiazole-4-carboxylic acid **124** are transformed by the action of such oxidants as $(SO_2Cl)_2O$ and Cl_2 into the bistriazolyl disulfides **125**.



124

125 45–65%

The second approach to the synthesis of 1,2,3-triazoles by the rearrangement of 1,2,3-thiadiazoles is the Cornforth rearrangement of 1,2,3-thiadiazoles containing a carbimine or thioimidolate function at position 4 of the ring [134, 136-140]. The 1,2,3-thiadiazolyl-4-carbimines **127** formed in the reaction of 1,2,3-thiadiazole-4-carbaldehydes **126** with primary amines rearrange to 1,2,3-thiadiazole-4-carbothioamides **128** [141-144].



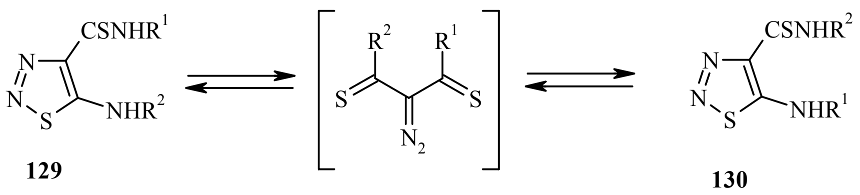
126

127

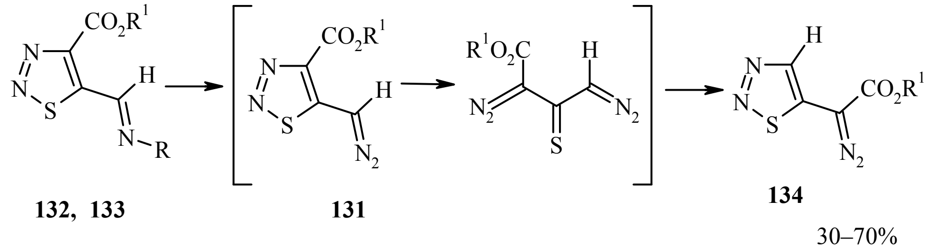
128 80–98%

R^1 = H, Ar, NR_2

One example of the rearrangement of the 1,2,3-thiadiazole ring to a 1,2,3-thiadiazole ring is the Cornforth rearrangement of 1,2,3-thiadiazole-4-carbothioamides **129** [145-148]. We showed that the rearrangement results in the formation of the isomeric 1,2,3-thiadiazole-4-carbothioamides **130**, differing in the position of the substituents R^1 and R^2. The rearrangement is a reversible equilibrium reaction, in which the position of the equilibrium is affected by the nature of the substituents and the solvent [148].

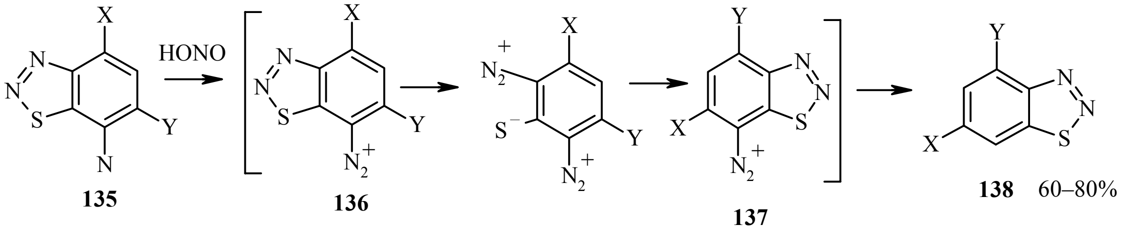


Another example is the L'Abbe rearrangement. It was shown [149] that 5-diazo-1,2,3-thiadiazoles **131**, generated either from the hydrazone **132** or from the oxime **133**, rearrange with the formation of the more stable diazo compound **134**.

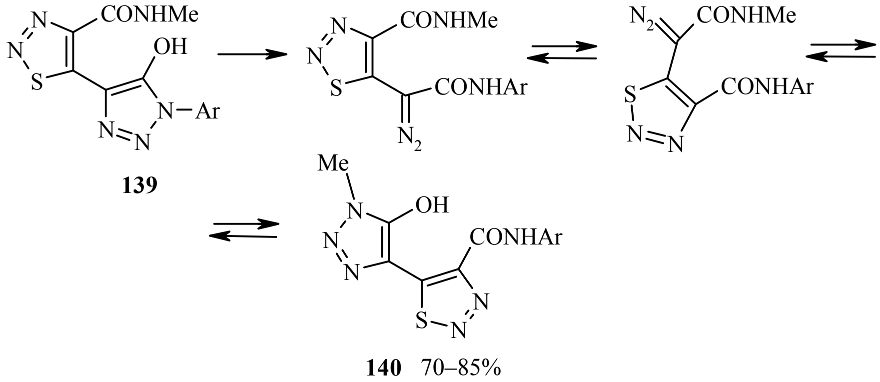


132 R = NHTs, **133** R = OH, **131–134** R^1 = H, Et

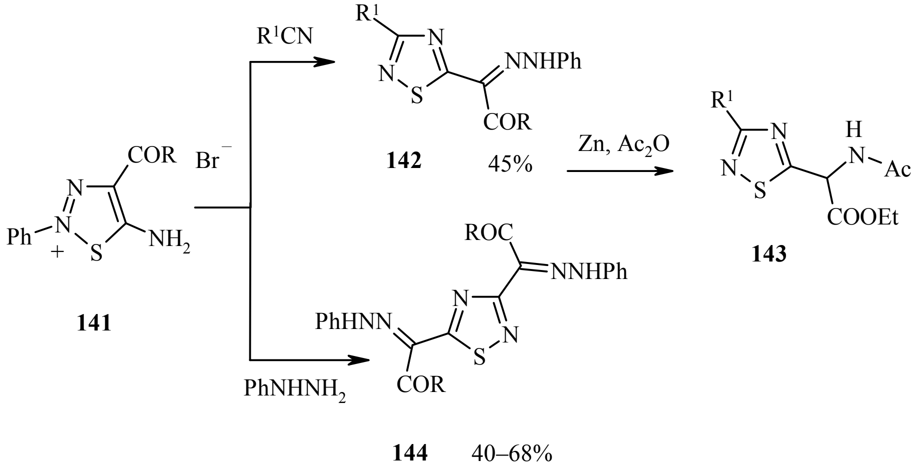
A similar rearrangement was described in [150, 151] for 1,2,3-benzothiadiazoles. It was found that during the diazotization of 7-amino-1,2,3-benzothiadiazole **135** the 1,2,3-benzothiadiazole-7-diazonium **136** that is formed rearranges to the isomeric 1,2,3-benzothiadiazole-7-diazonium **137** with subsequent loss of the diazo group and the formation of the benzothiadiazole **138**.



We described a rearrangement of the domino type involving the 1,2,3-thiadiazole and 1,2,3-triazole rings [152, 153]. One of the stages in the transformation of 5-(1,2,3-triazol-4-yl)-1,2,3-thiadiazoles **139** to the isomeric 5-(1,2,3-triazol-4-yl)-1,2,3-thiadiazoles **140** is rearrangement of the 1,2,3-thiadiazole ring with the participation of the diazo group at position 5, analogous with that discovered by L'Abbe.

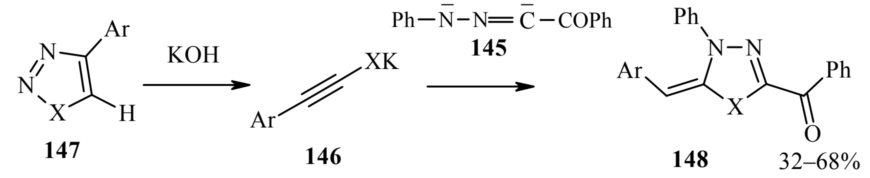


1,2,4-Thiadiazoles can also be obtained by the rearrangement of 1,2,3-thiadiazoles. Thus, the reaction of 5-amino-2-phenyl-1,2,3-thiadiazolinium bromides **141** with nitriles leads to the formation of 1,2,4-thiadiazoles **142** [128]. The hydrazone **142** was reduced to the amino derivative **143**.

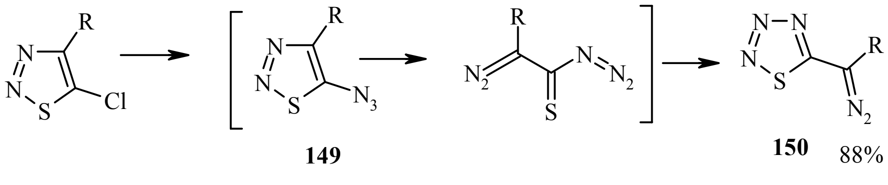


1,2,4-thiadiazoles **144** can be obtained by the transformation of the salt **141** by the action of phenylhydrazine [128].

The reaction of the nitrile imine **145** with potassium arylethynethiolate **146**, produced by the reaction of 5-aryl-1,2,3-thiadiazole **147** with potassium hydroxide, leads to the formation of 2-methylene-3-phenyl-1,3,4-thiadiazole **147** [154].

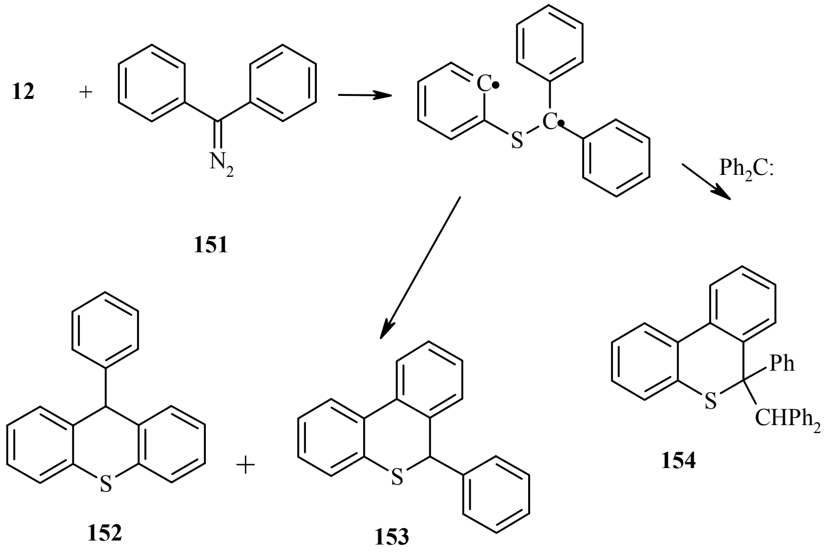


In [155, 156] it was shown that 5-azido-1,2,3-thiadiazole **149** rearranges to 5-diazo-1,2,3,4-thiatriazole **150**.

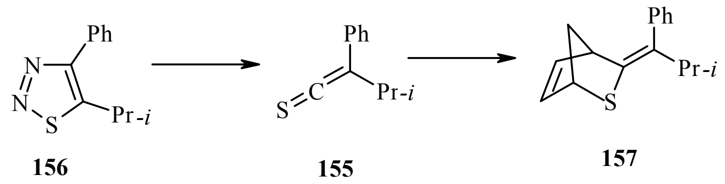


2.4. The Synthesis of Six-membered Rings

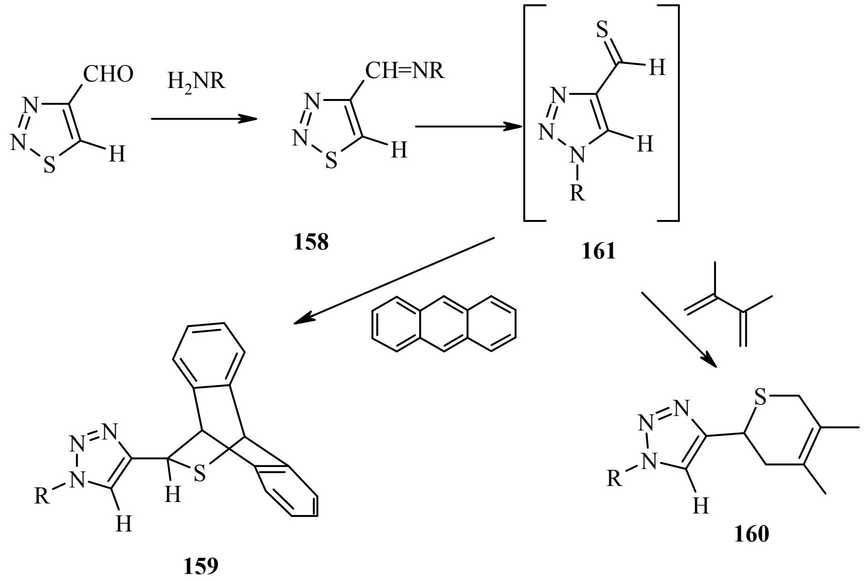
It was shown that thermal decomposition of the benzothiadiazole **12** in the presence of diphenyldiazomethane **151** gives a mixture of dibenzothiopyrans **152-154** [157].



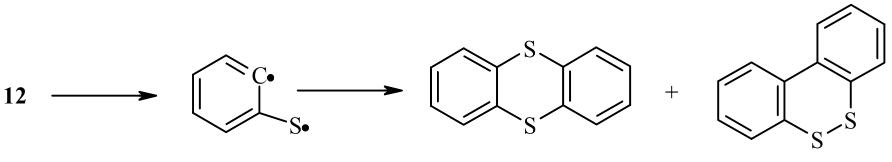
According to [158], the thioketene **155**, produced by the pyrolysis of 1,2,3-thiadiazole **156**, enters into [2+4] cycloaddition with cyclopentadiene with the formation of the bicycle **157**, the structure of which was confirmed by X-ray crystallographic analysis.



An interesting example of the synthesis of a thiopyran ring from 4-formyl-1,2,3-thiadiazole with retention of the N_2 fragment was described in [142]. The thiopyrans **159** and **160** were obtained by Diels–Alder reaction of the thiocarbaldehyde **161**, generated by Cornforth rearrangement of 1,2,3-thiadiazolecarbimine **158**, with anthracene or 2,3-dimethylbutadiene respectively.

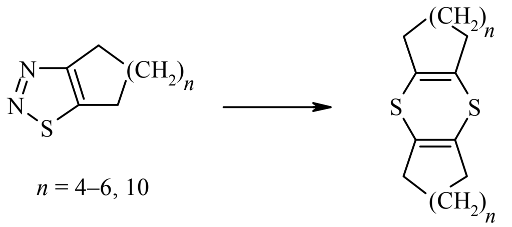


One of the main products from the thermolysis of 1,2,3-benzothiadiazoles **12** is thianthrene **162** [59, 68-72, 84, 100, 159, 160]. Its formation is explained by dimerization of the biradical **163** that is formed. In another version of the dimerization dibenzo[1,2]dithiin **164** is formed [68, 70-72, 100].



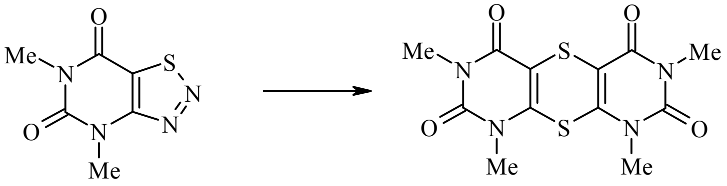
163 **162** **164**

The formation of 1,4-dithiins **165** and **166** is observed during the photolysis of 1,2,3-thiadiazoles [105, 161, 162].



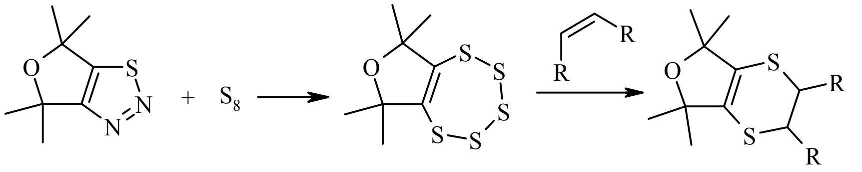
$n = 4–6, 10$

165 30–70%



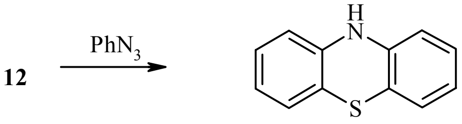
166 82%

When the 1,2,3-thiadiazole **167** is heated in the presence of sulfur, the cyclopolysulfides **168** are formed. Their photolysis in the presence of olefins leads to the 1,4-dithiins **169** [163].



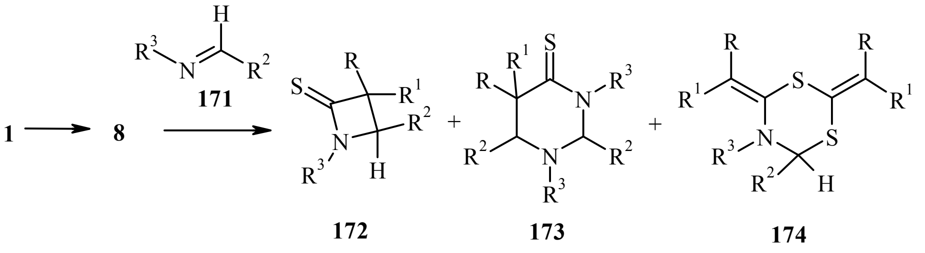
167 **168** **169** 50–70%

1,4-Dibenzothiazine **170** was obtained during the thermolysis of 1,2,3-benzothiadiazole **12** in the presence of phenyl azide [160].

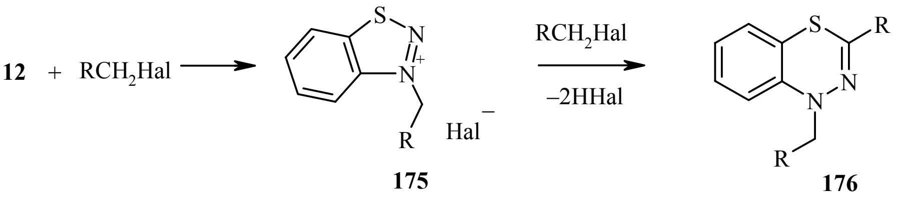


170 53%

The reaction of the thioketene, generated by the decomposition of the 1,2,3-thiadiazole **1**, with azomethines **171** leads to the formation of β-thiolactams **172**, pyrimidinethiones **173**, and 1,3,5-dithiazines **174** [92].

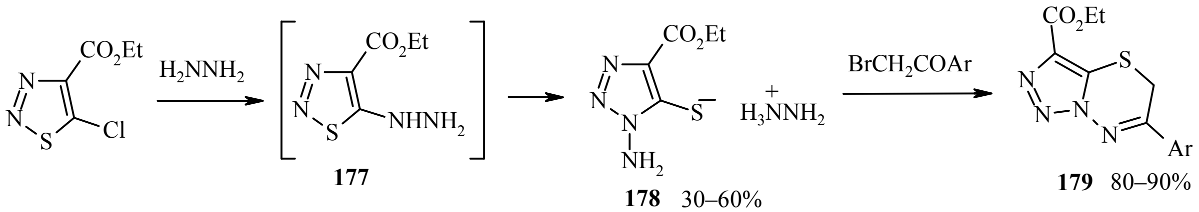


In the reaction of 1,2,3-benzothiadiazole **12** with alkyl halides the thiadiazole ring is alkylated at position 3. Reaction of the 3-alkylbenzothiadiazolium halide **175** with a second molecule of the alkyl halide leads to the formation of 1,3,4-thiadiazine **176** [164].

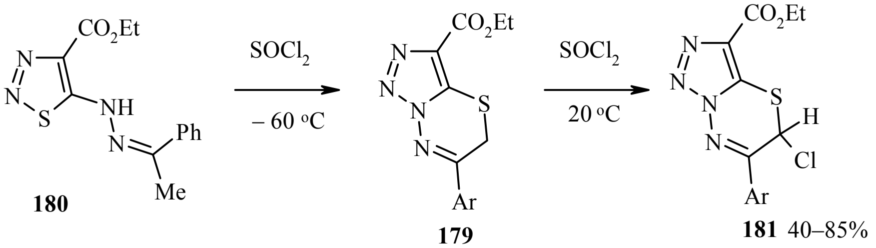


R = H, Me, Pr, $C_6H_4NO_2$-4, PhCO, CO_2Et

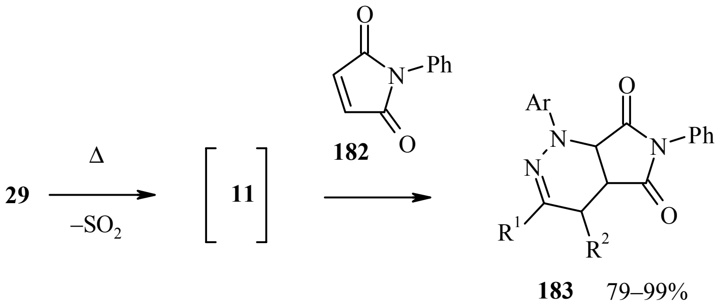
By tandem Dimroth rearrangement of 5-hydrazino-1,2,3-thiadiazole **177** and condensation of the obtained 1-amino-1,2,3-thiadiazole-5-thiolate **178** with α-bromoacetophenones L'Abbe was able to synthesize 5H-[1,2,3]triazolo[5,1-*b*][1,3,4]thiadiazines **179** [73].



During investigation of the reaction of 1,2,3-thiadiazolylhydrazones of acetophenones **180** with thionyl chloride we discovered that they are transformed into 5-chloro-5H-triazolothiadiazines **181** [165]. When the reaction was conducted at -60°C it was possible to isolate the intermediate 1,2,3-thiadiazolothiadiazines **179**.

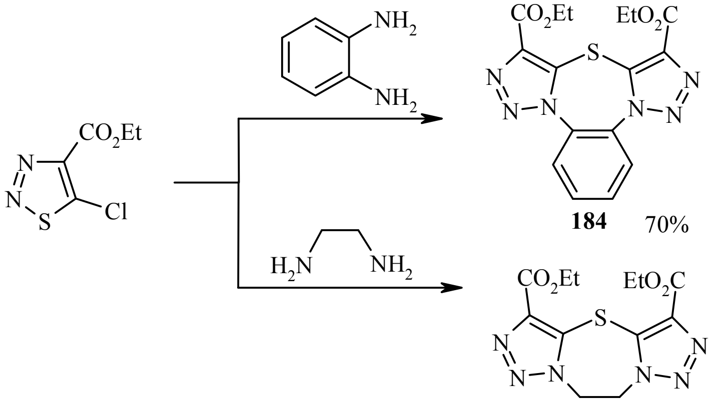


The 1,2-diazobutadiene **11** obtained from 1,2,3-thiadiazoline **29** enters into cycloaddition with the dienophile **182** with the formation of the condensed ring **183** [56].



2.5. The Synthesis of Seven-Membered Rings

We described an example of the transformation of 1,2,3-thiadiazoles leading to the formation of derivatives of 1,3,6-thiadiazepine in [166, 167]. It was found that the reaction of 5-chloro-1,2,3-thiadiazole with phenylenediamine and ethylenediamine led to bis[1,2,3]triazolo[1,5-*b*;5',1'-*f*]thiadiazepines **184** and **185**.



CONCLUSION

Thus, the derivatives of 1,2,3-thiadiazoles have great synthetic potential, particularly in the production of various types of heterocyclic systems. The transformations of 1,2,3-thiadiazoles make it possible to synthesize three-, four-, five-, six-, and seven-membered heterocycles. The decomposition of 1,2,3-thiadiazoles provides an original method for the synthesis of linear organic compounds such as thioamides, thioesters, hydroxamic acids, and others. These reactions have also been used for the synthesis of polymers and dendrimers with interesting technical characteristics.

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