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REVIEW

1-Substituted 5-Alkyl(aryl)sulfanyltetrazoles and Their Derivatives

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Abstract—The review analyzes published data on the synthesis, chemical properties, and application of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles. Specific attention is given to reactions of metalated 1-alkyl(aryl)-5-alkylsulfonyltetrazoles with electrophilic reagents as a general and highly stereoselective method for the preparation of functionally substituted olefins.

1. Introduction 447
2. Methods of Synthesis of 1-Substituted 5-Alkyl(aryl)sulfanyltetrazoles 447
  2.1. Alkylation of 1-Substituted Tetrazole-5-thiones 448
  2.2. Alkylation of 5-Alkyl(aryl)sulfanyltetrazoles 450
  2.3. Other Methods 451
3. Chemical Properties of 1-Substituted 5-Alkyl(aryl)sulfanyltetrazoles 452
  3.1. Electrophilic Substitution 452
  3.2. Nucleophilic Substitution 453
  3.3. Oxidation 455
  3.4. Reactions with Acids 456
  3.5. Other Reactions 456
4. Application 457
5. Conclusion 458

1. INTRODUCTION

Although tetrazole derivatives have long been studied, methods of synthesis and physical and chemical properties of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles have not received due attention [1–7]. Interest in 1-substituted 5-alkyl(aryl)sulfanyltetrazoles has considerably increased since mid 1980s when extensive works on improvement of methods for the preparation of these compounds and studies of their therapeutic activity have been initiated. The generally accepted views on the role of 5-alkyl(aryl)sulfanyltetrazoles in organic synthesis have changed radically after 1998 when Kocienski and co-workers [8, 9] have shown that 5-alkylsulfonyltetazoles may be used as highly efficient olefination reagents in the synthesis of natural biologically active compounds [10]. Since that time, the number of publications concerning 5-alkyl(aryl)sulfanyltetrazoles and their derivatives has increased considerably, indicating continuously growing interest in these compounds.

The present review discusses published data on the methods of preparation, chemical properties, and application of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles, the main attention being focused on the results of studies performed in the recent 10–15 years.

2. METHODS OF SYNTHESIS OF 1-SUBSTITUTED 5-ALKYL(ARYL)-SULFANYLTETRAZOLES

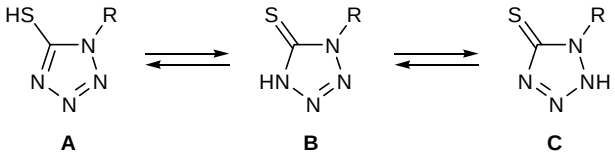
1-Substituted 5-alkylsulfanyltetrazoles can be obtained in several ways, among which alkylation of 1-substituted tetrazole-5-thiones and 5-alkylsulfanyltetrazoles is the most widely used. The other, less common methods include addition of 1-substituted

tetrazole-5-thiones to oxiranes and benzonitrilium *N*-4-nitrophenylimide and reactions of sodium azide with imidoyl chlorides generated from thiocarbamate derivatives.

2.1. Alkylation of 1-Substituted Tetrazole-5-thiones

Analysis of the known methods for the preparation of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles indicates that alkylation of 1-substituted tetrazole-5-thiones is one of the most promising. Its advantages are simple experimental procedures and accessibility of initial reagents and solvents. It is important that this reaction may be used as a convenient model for studying ambident heteroanions, for 1-substituted tetrazole-5-thiones can exist in several tautomeric forms (Scheme 1).

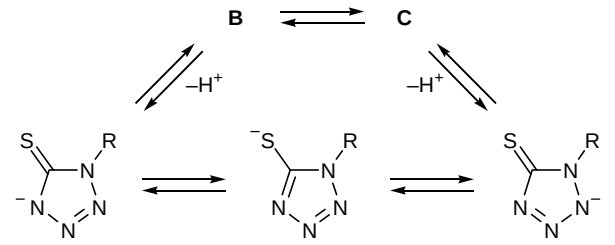
Scheme 1.



According to the available data, 1-substituted tetrazole-5-thiones in crystal and in solution exist preferentially in the thione form [11, 12]. Obviously, the state of tautomeric equilibrium **B** ⇌ **C** was not studied, but, according to some indirect data and the results of quantum-chemical calculations [13], 4*H*-tautomer **B** is more thermodynamically stable.

Tetrazolate ions formed by deprotonation of thiones **B** and **C** may be represented by canonical structures shown in Scheme 2.

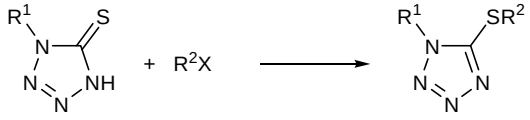
Scheme 2.



Reactions of such anions with alkylating and other electrophilic agents could give rise to three isomeric N^2-, N^4-, and S-substituted derivatives. However, because of the lack of systematic data, it is difficult to estimate the effect of the substrate structure, nature of alkylating agent, properties of the reaction medium, and other factors on the direction of alkylation of tetrazolate ions.

Even in early publications on the alkylation of 1-substituted tetrazole-5-thiones with alkyl halides and sulfuric acid esters it was noted that the reaction occurs at the sulfur atom, regardless of the substituent in position *1* of the heteroring [14–16] (Scheme 3). Later on, a detailed study of alkylation of numerous 1-substituted tetrazole-5-thiones confirmed the high regioselectivity of this reaction [9, 17–26].

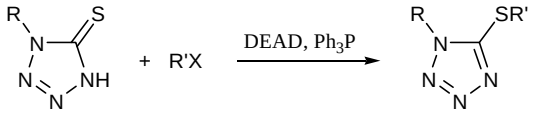
Scheme 3.



R^1 = Alk, Ar; X = Hlg, SO_4R^3.

In the last decade, apart from alkyl halides and sulfuric acid esters, alcohols were widely used as alkylating agents. The procedure was named after Mitsunobu [26]; acording to this procedure, tetrazole-5-thione is treated with an alcohol in the presence of diethyl azodicarboxylate (DEAD) or diisopropyl azodicarboxylate (DIAD) and triphenylphosphine [8, 24, 27–34] (Scheme 4).

Scheme 4.

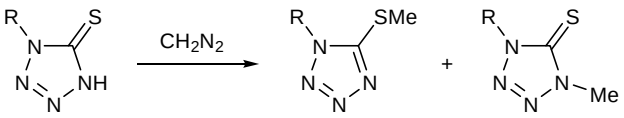


R = Alk, Ar; R' = Alk.

It should be noted that the alkylation of 1-substituted tetrazole-5-thiones with alcohols according to Mitsunobu yields only S-alkylation products. The alkylation direction changes only when diazoalkanes [35, 36] (Scheme 5) and compounds having an activated double bond [37] are used as alkylating agents (Scheme 6).

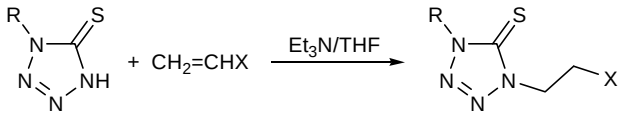
It still remains unclear what factors are responsible for the direction of alkylation of 1-substituted tetra-

Scheme 5.



R = Me, *t*-Bu.

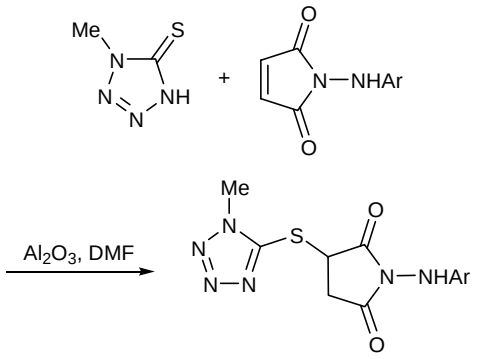
Scheme 6.



R = Ph, Bzl; X = CHO, COMe, COOMe, CN.

zole-5-thiones with unsaturated compounds. For example, Lippmann and Reifegerste [38] previously showed that the reaction of 1-phenyltetrazole-5-thione with unsaturated aldehydes yields S- rather than N-alkylation products. Analogous results were obtained in the alkylation of 1-methyltetrazole-5-thione with *N*–anilinomaleimides in the presence of alumina [39] (Scheme 7).

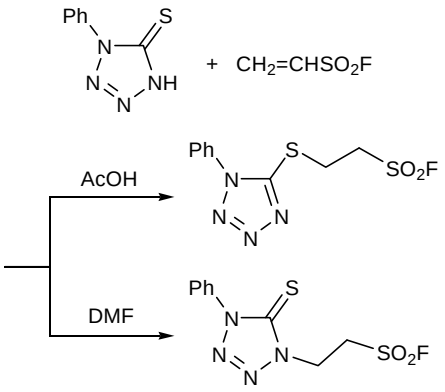
Scheme 7.



Ar = Ph, 4-$CF_3C_6H_4$, 2,4-$F_2C_6H_3$, 4-CNC_6H_4.

According to Nirinburg and Postovskii [40], the direction of alkylation of tetrazole-5-thiones with unsaturated compounds depends on the reactant ratio. The reaction of 1-phenyltetrazole-5-thione with an equimolar amount of acrylonitrile occurred exclusively at the sulfur atom, whereas with 8 equiv of the alkylating agent N-alkylation product was mainly formed.

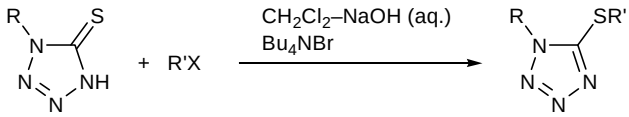
Scheme 8.



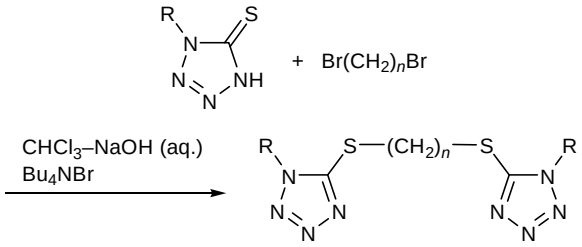
In some cases, the reaction direction depended on the structure of the alkylating agent and properties of the medium. For example, the alkylation of 1-phenyltetrazole-5-thione with ethenesulfonyl fluoride in acetic acid and in DMF afforded, respectively, the corresponding S- and N-substituted poducts in a high yield [41]. (Scheme 8). Obviously, only study of the reaction mechanism on a quantitative level would make it possible to draw some definite conclusions.

Very important results were obtained while studying the alkylation of 1-substituted tetrazole-5-thiones under conditions of phase-transfer catalysis [42–46]. Vast experimental data showed that alkylation of tetrazole-5-thiones with alkyl halides or dimethyl sulfate in the two-phase system chloroform–aqueous sodium hydroxide in the presence of quaternary ammonium salts leads to formation of the S-alkylation products in high yields (Scheme 9). The proposed procedure is general: it can be used to obtain both mono- and bis-tetrazoles.

Scheme 9.



R = Me, Ph, 4-$NO_2C_6H_4$, 4-$NO_2C_6H_4CH_2$; R' = Me, $(CH_2)_2Br$, CH_2CN, $(CH_2)_2CN$, CH_2COOH, CH_2COOEt, Bzl, 4-$NO_2C_6H_4CH_2$.



R = Me, Ph; *n* = 1–3.

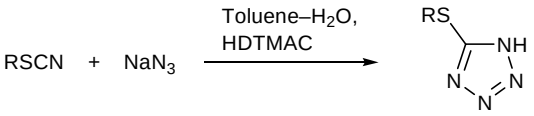
It was found that the direction of alkylation of ambident tetrazolate ions under conditions of phase-transfer catalysis does not depend on the substituent in position *1* of the heteroring, nature of the alkylating agent, and structure of phase-transfer catalyst. In all cases, the nucleophilic center in the substrate is the more readily polarizable sulfur atom. These results are very important. They provide a new insight into the problem of reactivity of ambident heteroanions, for the alkylation of such anions in two-phase systems is known to take different pathways [47–50].

Comparison of different methods for alkylation of 1-substituted tetrazole-5-thiones gives us grounds to believe that the procedure involving phase-transfer catalysis is the most efficient route to 1-substituted 5-alkyl(aryl)sulfanyltetrazoles. Apart from the advantages noted above, this method is attractive since other functional groups both in the substrate and in the reagent are not involved. This is very important for studies of natural biologically active compounds, specifically when the synthetic sequence includes olefination with the aid of 1-alkyl(aryl)-5-alkylsulfanyltetrazoles [10].

2.2. Alkylation of 5-Alkyl(aryl)sulfanyltetrazoles

Alkylation of 5-alkyl(aryl)sulfanyltetrazoles is one of the most poorly studied fields of the tetrazole chemistry. Obviously, the reasons are the lack of convenient methods for the preparation of 5-alkyl-(aryl)sulfanyltetrazoles and considerable difficulties in the separation of isomeric 1,5- and 2,5-disubstituted tetrazoles formed by alkylation. Until recently, almost the only method for the preparation of 5-alkyl(aryl)-sulfanyltetrazoles was addition of hydrazoic acid salts to the corresponding thiocyanates in DMF or aqueous dioxane [51, 52]. The situation has changed since 1998 when Le Blanc and Jursic have shown [53] that 5-alkyl(aryl)sulfanyltetrazoles can be obtained in high yield by reaction of thiocyanates with sodium azide under conditions of phase-transfer catalysis in the presence of hexadecyltrimethylammonium chloride (HDTMAC) (Scheme 10).

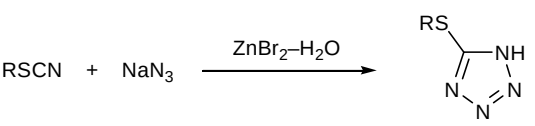
Scheme 10.



R = Alk, Ar.

Three years later, Demko and Sharpless proposed even more efficient procedure for the synthesis of such compounds via reaction of thiocyanates with sodium azide in water in the presence of zinc(II) bromide [54, 55] (Scheme 11). The results of their works has eliminated one of the main factors preventing for a long time extensive studies of 5-alkyl(aryl)sulfanyltetrazoles.

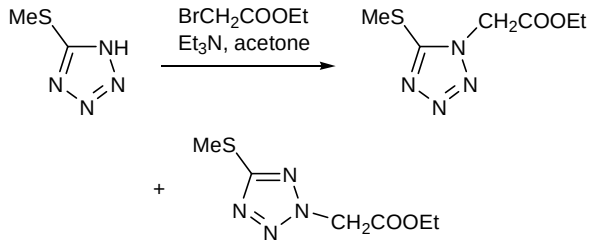
Scheme 11.



R = Me, Bzl.

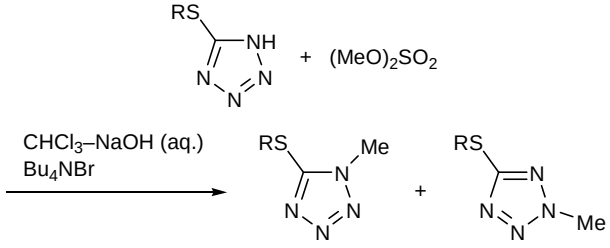
A pioneering study on the alkylation of 5-alkylsulfanyltetrazoles was performed more than 30 years ago by Raap and Howard [56]. The authors found that the reaction of 5-methylsulfanyltetrazole with ethyl bromoacetate gives isomeric N^1- and N^2-substituted derivatives at a ratio of 3:5 (Scheme 12). The selectivity of this reaction is low, which is typical of alkylation of 5-substituted tetrazoles [7, 57].

Scheme 12.



No appreciable change in the ratio of isomeric products was observed in the alkylation of 5-alkyl-(aryl)sulfanyltetrazoles under conditions of phase-transfer catalysis [58, 59] (Scheme 13).

Scheme 13.



R = Me, Bu, C_6H_{13}, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$.

The substituent in the substrate has no effect on the selectivity of the process, whereas the substituent nature was found to be significant in the alkylation of sulfur-free analogs [60]. Obviously, this difference may be interpreted in terms of an appreciable bridging effect of the sulfur atom, which essentially levels the electronic effect of substituent on the reaction center.

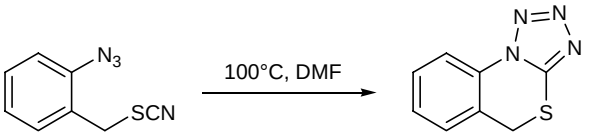
Insofar as the available information on physical and chemical properties of 1-alkyl(aryl)sulfanyltetrazoles is clearly insufficient, it is difficult to predict possible application of these compounds in the synthesis of

1-substituted 5-alkyl(aryl)sulfanyltetrazoles. However, we believe with a high degree of certainty that development of new improved procedures for the preparation of 5-alkyl(aryl)sulfanyltetrazoles (see above) could extend the potential of further studies on these compounds.

2.3. Other Methods

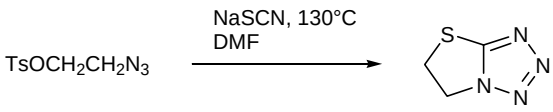
Among less common methods for the preparation of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles, the following must be noted: intramolecular [2+3]-cyclization of azido thiocyanates [55], reactions of 1-alkyl(aryl)tetrazole-5-thiones with ortho esters [61] and with *tert*-butyl alcohol in the presence of *N*,*N'*-dicyclohexylcarbodiimide (DCC) and copper(II) chloride [62], and some other reactions. Intramolecular [2+3]-cyclization of azido thiocyanates is a novel route to tetrazolethione derivatives. The cyclization occurs on heating to 100°C in DMF, and the corresponding cyclic sulfanyltetrazoles are formed in a high yield (Scheme 14).

Scheme 14.



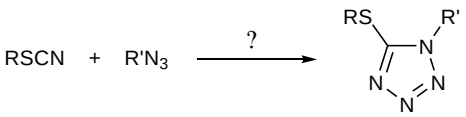
This procedure can readily be modified by using more accessible azidoalkyl *p*-toluenesulfonates instead of azido thiocyanates. In this case, the reaction is carried out in the presence of sodium thiocyanate (Scheme 15).

Scheme 15.



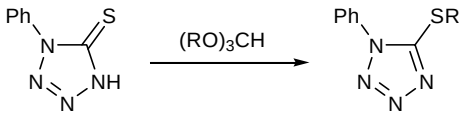
Obviously, such a way of building up a tetrazole ring is universal. Intermolecular [2+3]-cyclizations of thiocyanates with organic azides could lead to various 1-substituted 5-alkyl(aryl)sulfanyltetrazoles, as shown in Scheme 16.

Scheme 16.



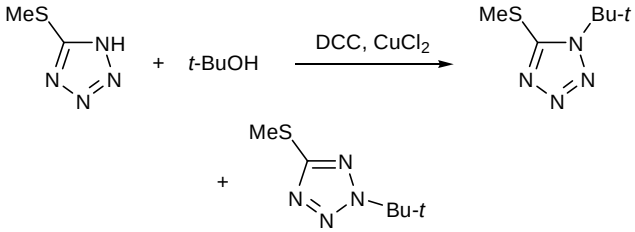
In some cases, syntheses of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles by reactions of the corresponding tetrazole-5-thiones with ortho esters [61] (Scheme 17), as well as with *t*-BuOH and DCC in the presence of copper(II) chloride (Scheme 18), may be fairly effective. However, separation of isomeric 1- and 2-*tert*-butyltetrazoles formed in the latter reaction may be difficult.

Scheme 17.



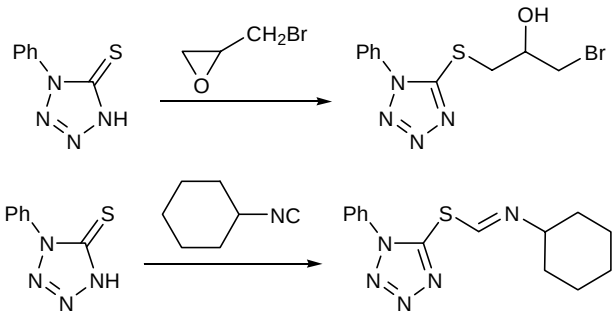
R = Me, Pr, Bu.

Scheme 18.

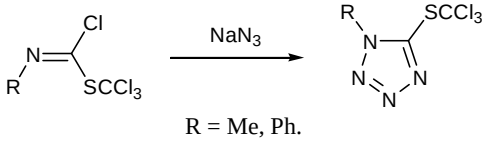


1-Substituted 5-alkyl(aryl)sulfanyltetrazoles were also synthesized by addition of tetrazole-5-thiones to oxiranes [17, 63] and isocyanides [64] (Scheme 19), by reaction of imidoyl chlorides with sodium azide [65] (Scheme 20), by reaction of tetrazolethiones with benzonitrilium *N*-4-nitrophenylimide [66] (Scheme 21), and by reaction of 1-aryltetrazole-5-thiones with chlorodifluoromethane in aqueous dioxane in the presence of potassium hydroxide [67] (Scheme 22).

Scheme 19.

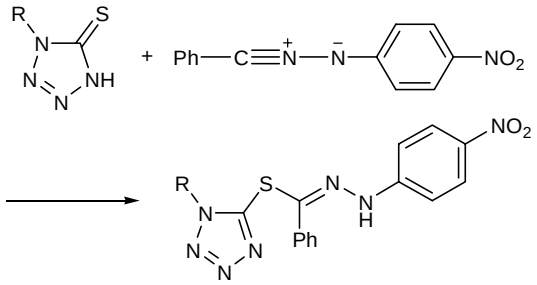


Scheme 20.



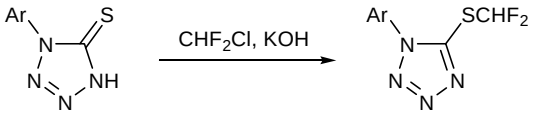
R = Me, Ph.

Scheme 21.



R = Me, 4-MeC_6H_4, 4-$NO_2C_6H_4$.

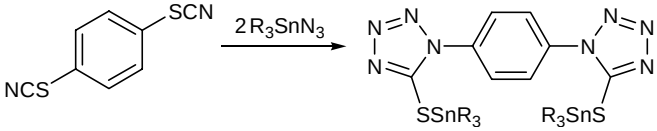
Scheme 22.



Ar = Ph, 4-MeC_6H_4, 2-MeC_6H_4.

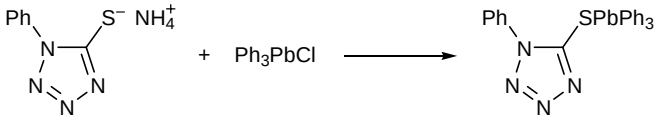
Finally, we should note, at least briefly, metalated sulfanyltetrazoles in which the metal atom is directly attached to sulfur, although discussion on the methods of preparation and chemical properties of such derivatives goes beyond the scope of the present review. In the recent years, an exceptionally strong interest has arisen in the chemistry of supramolecular structures [68, 69]. As shown in [70–72], some metalated sulfanyltetrazoles are capable of giving rise to such structures. Examples of the synthesis of metal derivatives are shown in Schemes 23 and 24 [71, 72].

Scheme 23.



R = Me, Et, Bu, Ph.

Scheme 24.



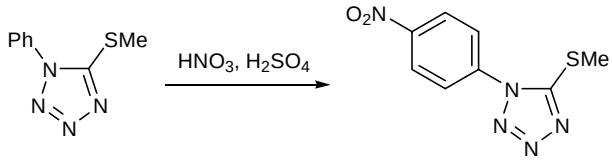
3. CHEMICAL PROPERTIES OF 1-SUBSTITUTED 5-ALKYL(ARYL)SULFANYLTETRAZOLES

Extensive studies on the properties of 1-substituted 5-aryl-(alkyl)sulfanyltetrazoles have started in the mid 1990s. This problem almost was not discussed in early reviews on the chemistry of tetrazoles. Therefore, systematization of numerous experimental data on various aspects of the chemistry of sulfanyltetrazoles should be useful for estimation of prospects in the application of these compound in organic synthesis and in the preparation of pharmacologically active substances. This section describes electrophilic and nucleophilic substitution in the series of sulfanyltetrazoles, their oxidation, reactions with acids, and some other transformations.

3.1. Electrophilic Substitution

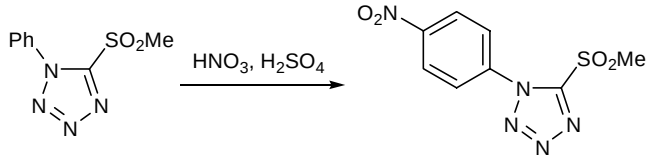
Scott *et al*. [73] were the first to report on electrophilic substitution in 1-substituted 5-alkyl(aryl)sulfanyltetrazoles. The authors studied the nitration of 5-methylsulfanyl-1-phenyltetrazole with a mixture of nitric and sulfuric acids at 0°C and obtained 5-methylsulfanyl-1-(4-nitrophenyl)tetrazole in high yield (Scheme 25).

Scheme 25.



Much later, it was shown that the reaction time can be shortened considerably without loss in the product yield [74]. The procedure turned out to be effective in the nitration of 5-methylsulfonyl-1-phenyltetrazole [74] (Scheme 26).

Scheme 26.

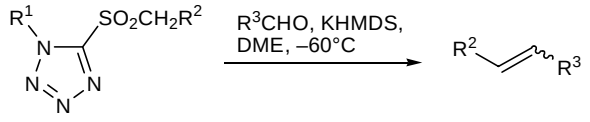


Exceptionally important results in studying electrophilic substitution in the series of sulfanyltetrazoles were obtained by Kocienski and co-workers who showed that reactions of metalated 1-substituted 5-alkylsulfonyltetrazoles with aldehydes lead to formation of *trans*-1,2-disubstituted alkenes with high yield and stereoselectivity [8, 9]. Subsequently, this olefination procedure was referred to as modified Julia's olefination [10]. It is more advantageous than the original procedure proposed by Julia [75] due to considerably higher stereoselectivity. These studies gave an impetus to wide application of 1-substituted

5-alkylsulfonyltetrazoles in numerous syntheses of natural biologically active compounds [10].

The reaction is carried out by treatment of a 1-alkyl-(aryl)-5-akylsulfonyltetrazole with hexamethyldisilazane sodium or potassium salt (NaHMDS or KHMDS) in dimethoxyethane (DME) at –60°C, followed by addition of the corresponding aldehyde (Scheme 27).

Scheme 27.



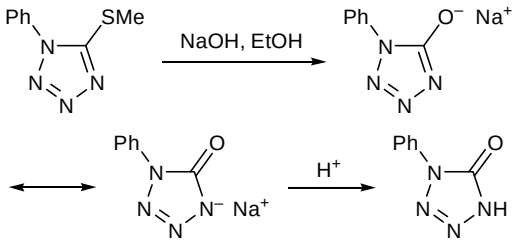
R^1 = *t*-Bu, Ph.

The yield and isomer ratio of the olefins thus formed strongly depend on the substituent in position *1* of the heteroring. In going from R^1 = *t*-Bu to R^1 = Ph (R^2 being the same), the overall yield of isomeric olefins decreases, but the fraction of the *E* isomer increases.

3.2. Nucleophilic Substitution

Nucleophilic substitution in sulfanyltetrazoles can occur at the endocyclic carbon atom and in the side chain. In the simplest case, heating of 5-methylsulfanyl-1-phenyltetrazole in a boiling 5% alcoholic solution of sodium hydroxide gives 84% of 1-phenyltetrazol-5-one [74] (Scheme 28).

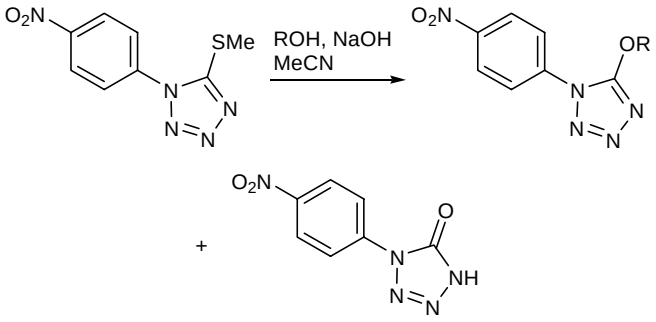
Scheme 28.



Under milder conditions, e.g., at 35°C, no replacement of the methylsulfanyl group was observed. Introduction of a nitro group into the 1-phenyl substituent considerably increases the reactivity with respect to O-nucleophiles. Treatment of 5-methylsulfanyl-1-(4-nitrophenyl)tetrazole with a 15% solution of sodium hydroxide in 25% aqueous ethanol at 35°C leads to formation of 1-(4-nitrophenyl)tetrazol-5-one in 70% yield.

The methylsulfanyl group in 5-methylsulfanyl-1-(4-nitrophenyl)tetrazole is replaced under mild conditions by the action of alkoxide ions. The reaction occurs in an alcohol–acetonitrile mixture at 20°C in the presence of sodium hydroxide. However, in all cases 1-(4-nitrophenyl)tetrazol-5-one is formed (Scheme 29).

Scheme 29.

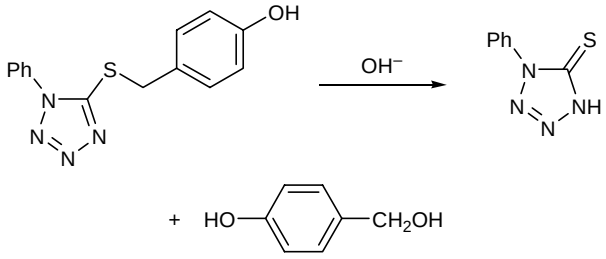


R = Me, Et, *i*-Pr, Bu, Ph.

It should also be noted that such O-nucleophiles as phenoxide ion and N-nucleophiles formed by deprotonation of imidazole and benzimidazole do not react with 5-methylsulfanyl-1-(4-nitrophenyl)tetrazole [74].

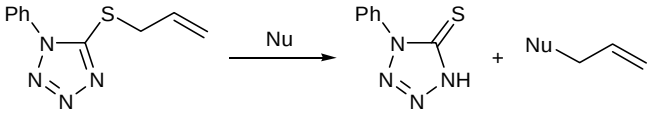
In some cases, the site of nucleophilic substitution in 1-substituted 5-alkylsulfanyltetrazoles depends on the structure of the substituent at the sulfur atom [18, 76]. This may be illustrated most clearly with isomeric 5-(hydroxybenzylsulfanyl)-1-phenyltetrazoles [76]. 5-(2-Hydroxybenzylsulfanyl)- and 5-(4-hydroxybenzylsulfanyl)-1-phenyltetrazoles are smoothly hydrolyzed in a dilute aqueous solution of sodium hydroxide at 18–20°C (Scheme 30).

Scheme 30.



However, 5-(3-hydroxybenzylsulfanyl)-1-phenyltetrazole remains intact under the same conditions. Treatment of the latter with a 10% aqueous solution of sodium hydroxide at elevated temperature yields 1-phenyltetrazol-5-one. One more example of the effect of substituent on the sulfur atom is the reaction of 5-allylsulfanyl-1-phenyltetrazole which such nucleophiles as Grignard compounds, diethyl malonate sodium salt, and arenesulfinates [77, 78] (Scheme 31).

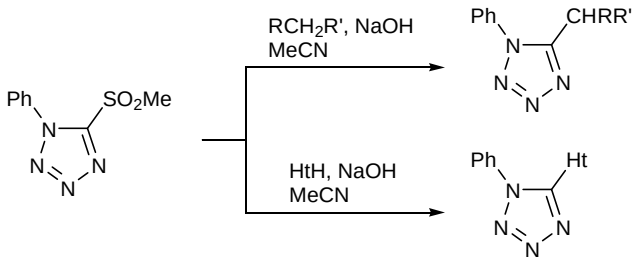
Scheme 31.



Nu = RMgX, $(ROOC)_2CH^-$, $ArSO_2^-$.

1-Aryl-5-methylsulfonyltetrazoles are characterized by considerably higher reactivity toward various nucleophiles. The methylsulfonyl group therein is smoothly replaced by the action of both C- and N-nucleophiles [39, 74] (Scheme 32).

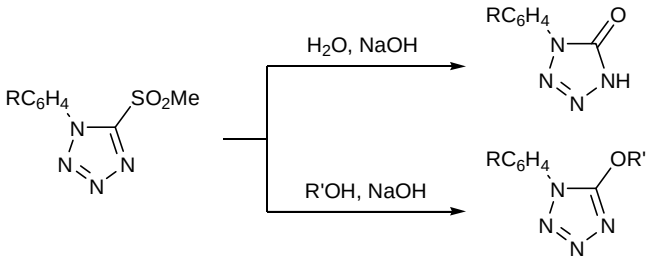
Scheme 32.



R = R' = CN; R = CN, R' =COOEt; R= CN, R' = 4-$NO_2C_6H_4$.

Replacement of the methylsulfonyl group in 5-methylsulfonyl-1-phenyl- and 5-methylsulfonyl-1-(4-nitrophenyl)tetrazoles by the action of O-nucleophiles readily occurs at 20°C (Scheme 33).

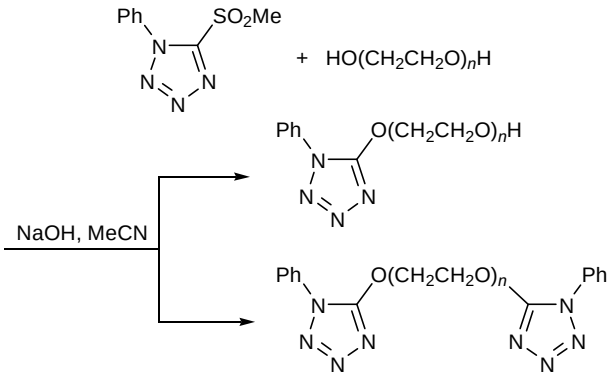
Scheme 33.



R = H, 4-NO_2; R' = Me, Et, Pr, *i*-Pr, Bu, Bzl, 4-MeC_6H_4, Ph, 4-$NO_2C_6H_4$.

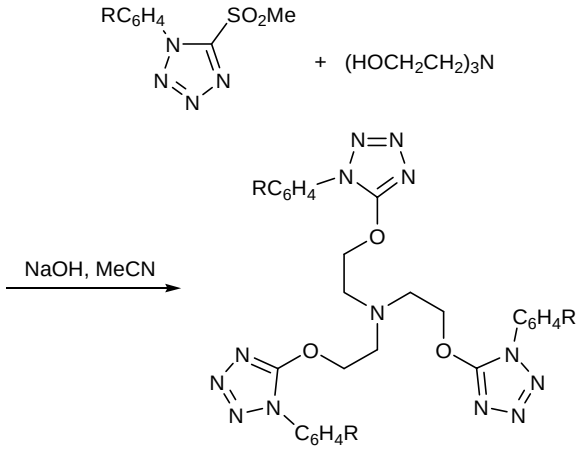
Here, multibasic functionally substituted alcohols, e.g., ethylene glycol, diethylene glycol, and triethylene glycol, as well as tris(2-hydroxyethyl)amine, can be used as O-nucleophiles [79]. Depending on the reactant ratio, the reaction with glycols gives mono- or disubstituted products (Scheme 34). Reactions of 1-aryl-5-methylsulfonyltetrazoles with tris(2-hydroxyethyl)amine lead to formation of polytetrazoles which can be used in the synthesis of tetrazole-containing dendrimers [80] (Scheme 35).

Scheme 34.



n = 1, 2, 3.

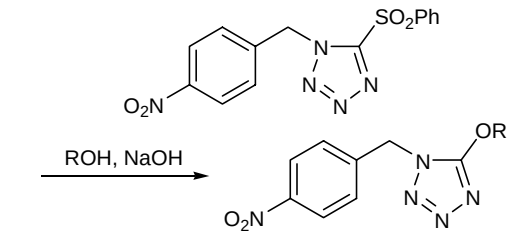
Scheme 35.



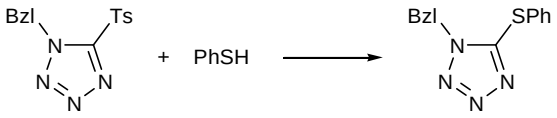
R = H, 4-NO_2.

According to the most recent data [59, 81], the arylsulfonyl group in 1-substituted 5-arylsulfonyltetrazoles is readily replaced by O- and S-nucleophilic species. The reaction occurs at room temperature, and the yield of the corresponding functionally substituted tetrazoles attains 77–95% (Scheme 36).

Scheme 36.

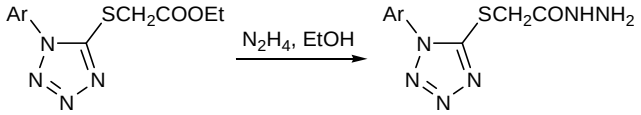


R = Me, Et, Ph.



Unfortunately, there are almost no published data on nucleophilic substitution in the side chain of sulfanyltetrazoles. One of the rare examples of such transformations is shown in Scheme 37: The reaction of ethyl 2-(1-aryltetrazol-5-ylsulfanyl)acetate with hydrazine afforded the corresponding hydrazide [16].

Scheme 37.

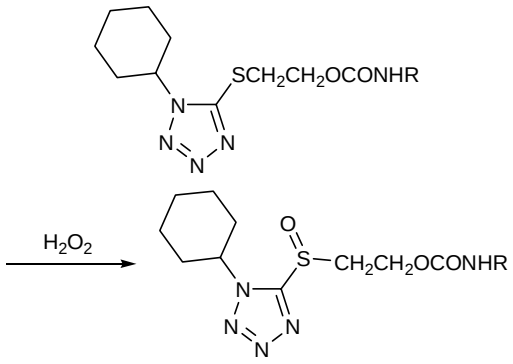


3.3. Oxidation

The tetrazole ring is very stable to oxidation [2, 4]. Reactions of tetrazoles with oxidants usually involve functional groups located in the side chain. Analogous relations are typical of 1-substituted 5-alkyl(aryl)-sulfanyltetrazoles; their oxidation has been studied in sufficient detail. In all cases, treatment of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles with oxidants leads to formation of the corresponding sulfoxides or sulfones. Commonly used oxidants are hydrogen peroxide [27, 29–31, 82–86], potassium permanganate [15, 39, 59], Oxone [9, 34], and *m*-chloroperoxybenzoic acid (MCPBA) [8, 9, 20, 23–25, 28, 32, 87–89]; among these, hydrogen peroxide and MCPBA are used most widely.

The oxidation of 1-substituted 5-alkylsulfanyl-tetrazoles with 30% hydrogen peroxide gives the corresponding sulfoxides [82] (Scheme 38).

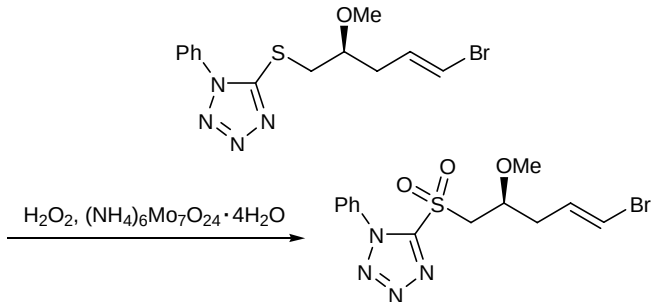
Scheme 38.



R = Ph, 3-ClC_6H_4.

Under analogous conditions but in the presence of molybdenum catalyst, 5-alkylsulfonyltetrazoles were obtained, regardless of the substrate nature [30, 82] (Scheme 39).

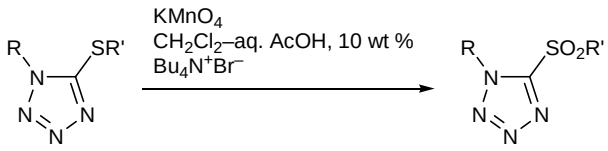
Scheme 39.



The yields of the oxidation products attain 71–89% [27, 29, 30, 82, 83].

Oxidation of 1-substituted 5-alkyl(aryl)sulfanyl-tetrazoles with potassium permanganate provides a simple and convenient route to the corresponding sulfonyl derivatives. From the preparative viewpoint, the reaction is the most effective under conditions of phase-transfer catalysis [39, 59] (Scheme 40).

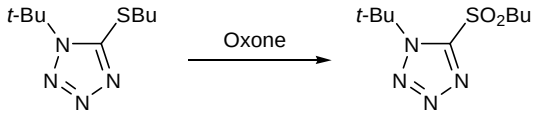
Scheme 40.



R = Me, 4-$NO_2C_6H_4CH_2$, Ph; R' = Me, $(CH_2)_2CN$, Bzl, Ph.

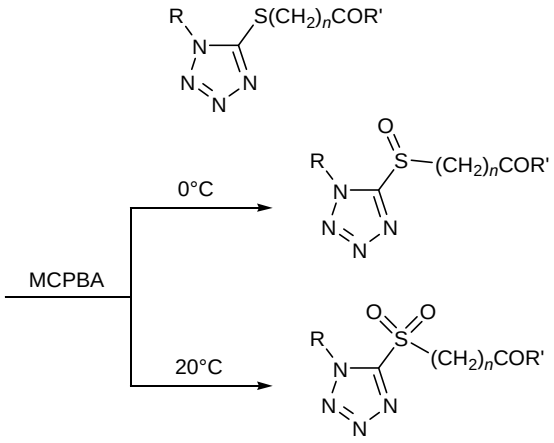
Relatively recently, it was proposed to use Oxone as oxidant. As noted in [9], the yield of the sulfonyl derivative in the oxidation with Oxone depends on the structure of the substituent at the sulfur atom. For example, treatment of 1-*tert*-butyl-5-butylsulfanyltetrazole with Oxone in methanol gives 81% of butyl 1-*tert*-butyltetrazol-5-yl sulfone (Scheme 41), while the yield of the corresponding sulfone in the oxidation of 5-benzylsulfanyl-1-*tert*-butyltetrazole is only 12%.

Scheme 41.



m-Chloroperoxybenzoic acid is an oxidant which could give rise to both 5-alkylsulfinyl and 5-alkyl-sulfonyl tetrazole derivatives. The oxidation of 1-substituted 5-alkylsulfanyltetrazoles with MCPBA in methylene chloride or chloroform at 0°C leads to the corresponding sulfoxides, while at 18–20°C 5-alkyl-sulfonyltetrazoles are formed [20, 88] (Scheme 42).

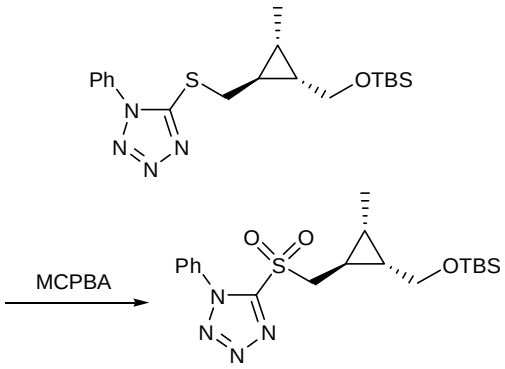
Scheme 42.



R = Me, Ph; R' = C_6H_{11}, Ph; *n* = 1–3.

One more important advantage of MCPBA as oxidant is that other functional groups present in the substrate remain intact, which may be crucial in the oxidation of polyfunctional sulfanyltetrazoles [10, 32, 89] (Scheme 43).

Scheme 43.

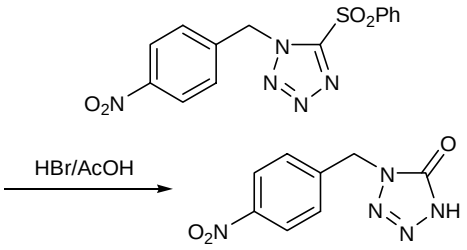


3.4. Reactions with Acids

The stability of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles in aqueous mineral acid solutions was not studied. Also, no studies were performed on the basicity of these compounds. The lack of relevant data strongly complicates examination of chemical transformations of sulfanyltetrazoles in acid medium. Probably, this is the reason why the information on the behavior of sulfanyltetrazoles in acid solutions is very scanty.

It was recently showed that treatment of 5-methylsulfonyl-1-(4-nitrobenzyl)- and 5-phenylsulfonyl-1-(4-nitrobenzyl)tetrazoles with a mixture of hydrobromic and acetic acids leads to formation of 1-(4-nitrobenzyl)tetrazol-5-one as a result of hydrolysis [59] (Scheme 44).

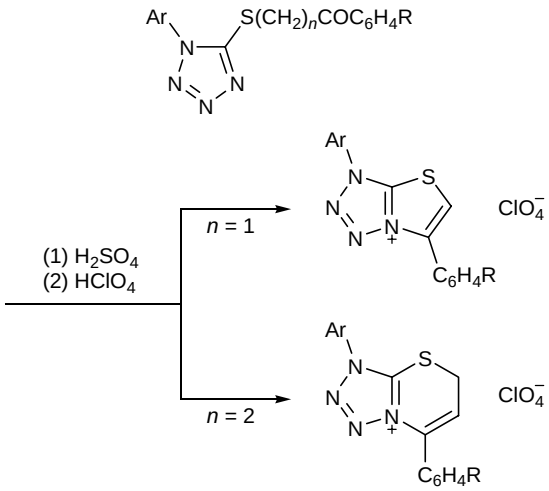
Scheme 44.



R = Me, Ph.

Alper and Stout [17, 90] obtained very important results while studying transformations of some 1-aryl-5-(ω-aroylalkylsulfanyl)tetrazoles in concentrated sulfuric acid. After prolonged (for several days) stirring of solutions of these compounds in concentrated sulfuric acid at 18°C, the corresponding thiazolo[3,2-*d*]-tetrazolium and tetrazolo[5,4-*b*][1,3]thiazinium salts were formed, which were isolated as perchlorates (Scheme 45). Presumably, the process involves protonation of the substrate at the side-chain carbonyl group, and the carbenium ion thus formed is stabilized via intramolecular ring closure with quaternization of the N^4 atom.

Scheme 45.



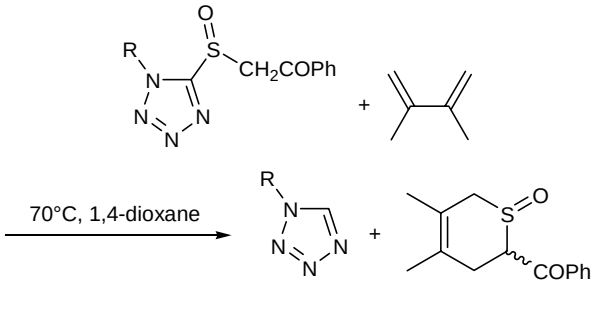
R = H, 4-F, 4-Cl, 4-NO_2.

3.5. Other Reactions

This section describes some chemical transformations of 1-substituted 5-alkylsulfanyltetrazoles, only a few examples of which have been reported. Therefore, such reactions cannot be classed with respect to

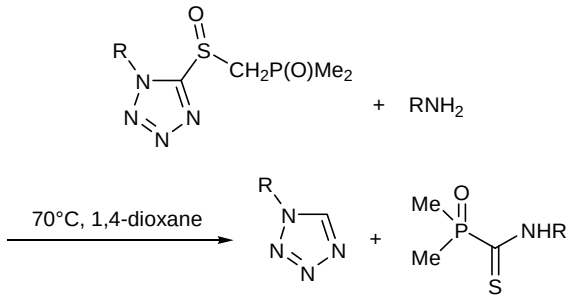
their mechanism or product nature. First of all, thermal transformations of 1-substituted 5-alkylsulfinyltetrazoles in the presence of 2,3-dimethyl-1,3-butadiene [88] (Scheme 46) and various amines [91] (Scheme 47) should be noted.

Scheme 46.



R = Me, Ph.

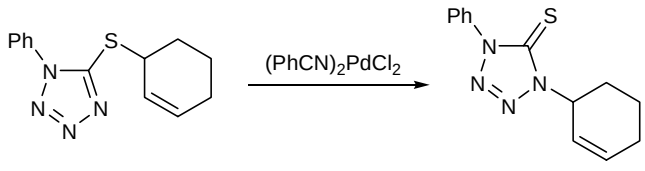
Scheme 47.



R = Ph, Bzl.

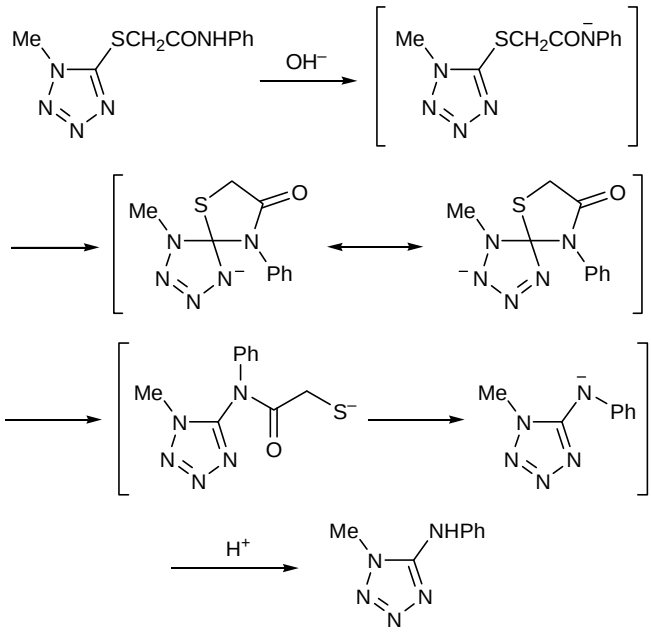
Isomerization of 5-(2-cyclohexenylsulfanyl)-1-phenyltetrazole in the presence of palladium catalyst [19] (Scheme 48) and Smiles rearrangements of 5-alkylsulfanyl-, 5-alkylsulfinyl-, and 5-alkylsulfonyl-1-methyltetrazoles [92, 93] (Scheme 49) were reported.

Scheme 48.

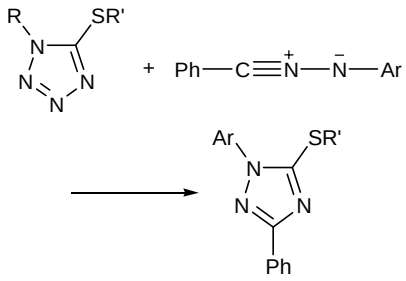


Finally, the transformation of 1-substituted 5-alkylsulfanyltetrazoles into 5-alkylsulfanyl-1,2,4-triazoles by the action of benzonitrilium *N*-4-nitrophenylimide [94] (Scheme 50) and quaternization of 1-alkyl-5-methylsulfanyltetrazoles [5, 35] (Scheme 51) are worth noting.

Scheme 49.

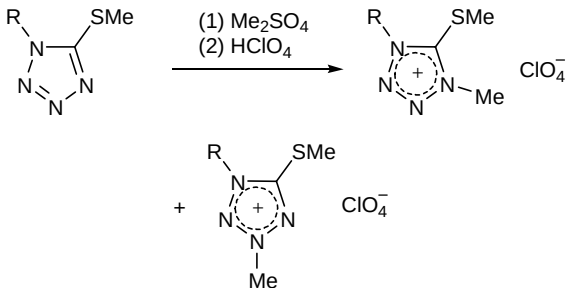


Scheme 50.



R = Me, Ph; R' = Me, Et, *i*-Pr.

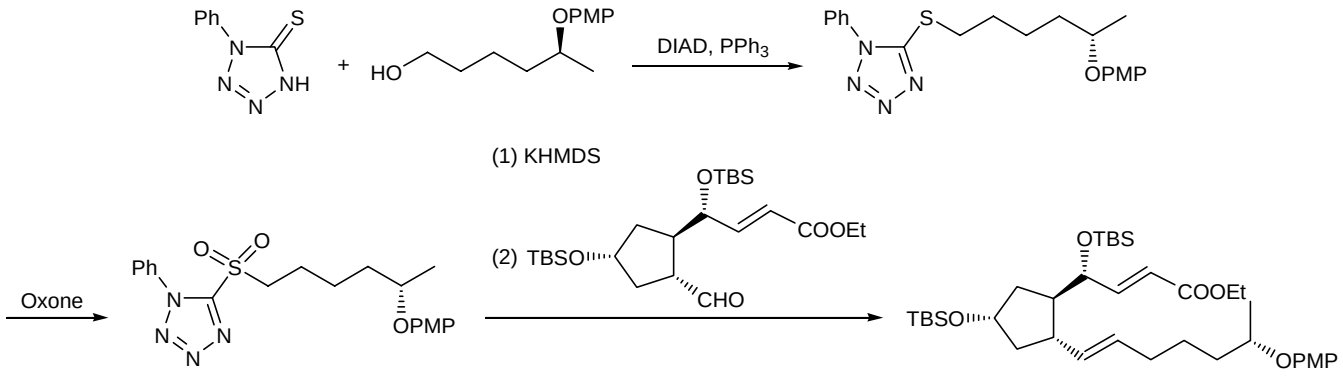
Scheme 51.



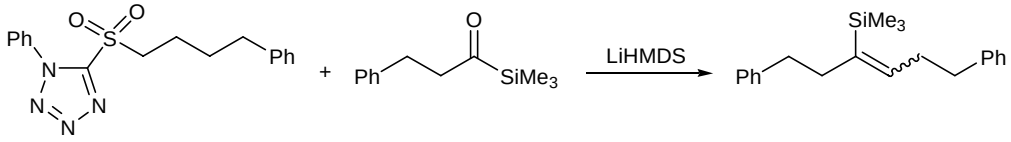
4. APPLICATION

Sulfanyltetrazoles are commonly used as medicines and components for data recording systems. Among pharmaceutical agents, we should primarily note highly efficient and widely used in practice β-lactam antibiotics of the cephalosporin and cephamycin series, namely Cefoperazone sodium [95], Moxalactam

Scheme 52.



Scheme 53.



[96, 97], Cefminox [98], Flomoxef [97], and some others [99–102]. Compounds exhibiting a high antituberculous [23, 103] and antimycobacterial activity [21, 42] were also found in the substituted sulfanyltetrazole series. Sulfanyltetrazoles were used as a basis for building up medical preparations for treatment of stomach ulcer [20, 87], cerebral ischemia [104], and some other diseases [105, 106].

As components for data recording systems, sulfanyltetrazoles are most widely used in developing compositions for treatment of multilayer color photographic materials [107], in manufacture of negative color photographic materials for scanning purposes [108], and in some other cases [109]. Földényi [22] recently reported on the possibility of using 1-alkyl-5-sulfanyltetrazoles as fungicides.

It should be emphasized that the scope of application of substituted sulfanyltetrazoles is not confined to medical chemistry and chemistry of photographic materials. In the recent years, new important ways of utilization of these compounds in organic synthesis have been proposed. This stems from advances in studying reactions of metalated 1-substituted 5-alkylsulfonyltetrazoles with electrophilic reagents, which lead to formation of olefins.

Starting from 1998, this olefination procedure has been widely used in the synthesis of biologically active compounds of natural origin. Vast experimental data on this topic, published until 2001 inclusively, have been reviewed in [10]. The most recent data obtained in the last two years are discussed below.

The strategy of application of 5-alkylsulfonyl-1-phenyltetrazoles in the preparation of natural biologically active compounds is clearly demonstrated with the synthesis of (+)-Brefeldin A as an example [34] (Scheme 52). Its total synthesis is a multistep process, one step of which is olefin formation from the corresponding alcohol and aldehyde. The olefination reaction is characterized by high stereoselectivity: *E/Z* ratio is larger than 12:1, and the yield is 81%.

Analogous approach was utilized in the synthesis of (+)-Thiazinotrienomycin E [28], Amphidinolide A [26], (+)-Zampanolide [85], Ionomycin [110], and other compounds of this series [30, 86, 111–120].

In addition, it should be noted that reactions of metalated 5-alkylsulfonyl-1-phenyltetrazoles with acylsilanes can be used for the preparation of vinylsilanes [121] (Scheme 53). Here, the overall yield attains 93%, and the *E/Z* isomer ratio is 9:6.

Other applications of 1-substituted 5-alkyl(aryl)-sulfanyltetrazoles in organic synthesis include preparation of thiazolium salts (see above) [17, 90] and difficultly accessible 6-substituted 3,4-dimethyl-5,6-dihydro-2*H*-thiopyran 1-oxides [88].

5. CONCLUSION

The history of studies on 1-substituted 5-alkyl-(aryl)sulfanyltetrazoles amounts to a little more than four decades. This period was insufficient to finally formulate main trends in the development of the chemistry of these compounds. Nevertheless, some

promising methods for the synthesis of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles and their derivatives, as well as ways of their utilization in organic synthesis and medical practice, may be pointed out even now.

Analysis of the known methods for the preparation of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles showed that, apart from the Mitsunobu alkylation of tetrazole-5-thiones with alcohols (which requires fairly expensive reagents), alkylation of the same substrates with alkyl halides and dialkyl sulfates under conditions of phase-transfer catalysis should be regarded as the simplest and most effective procedure. Among methods for the preparation of substituted sulfanyltetrazoles (studies of which are now in the initial stage), we should emphasize [2+3]-cycloaddition of thiocyanates and azides, leading to 1-substituted 5-alkyl(aryl)sulfanyltetrazoles in one step.

Of particular interest are recently discovered transformations of 1-substituted 5-alkylsulfonyltetrazoles by the action of electrophiles as a stereoselective route to olefins. Wide application of this reaction in the synthesis of various natural compounds made it possible to step much forward in the field of studying methods of synthesis, structure, chemical properties, and biological activity of such substrates.

It is now quite obvious that reactions of metalated 1-substituted 5-alkylsulfonyltetrazoles with electrophilic reagents provide a universal method for the preparation of functionally substituted olefins. From the practical viewpoint, it is reasonable to expect new important results in the synthesis of 1-substituted 5-alkyl(aryl)sulfanyltetrazoles possessing a high antibacterial and antituberculous activity.

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