Russian Chemical Reviews **65** (4) 307 – 314 (1996)
© 1996 Russian Academy of Sciences and Turpion Ltd

UDC 547.732

The tautomerism of heterocyclic thiols. Five-membered heterocycles

E D Shtefan, V Yu Vvedenskii

Contents

I.	Introduction	307
II.	Furan-, thiophene- and selenophene-thiols	307
III.	5-Mercaptopyrazoles	307
IV.	Imidazolethiones and 1,3-oxazole-2-thiones	308
V.	Thiazole-2-thiones	308
VI.	1,3,4-Oxadiazolethiones and 1,3,4-thia(selena)diazolethiones	308
VII.	5-Mercapto-1,3,4-thiadiazole-2-thiones and 1,2,4-thiadiazole-3,5-dithione	309
VIII.	1,2,4-Triazolethiones	310
IX.	Tetrazolethiones	311

Abstract. Data on the tautomerism of five-membered heterocyclic thiols and its effect on the behaviour of these compounds in different chemical reactions are surveyed. The bibliography includes 113 references.

I. Introduction

The tautomerism possible in heterocyclic thiols imparts a considerable diversity to their properties compared with those of aromatic thiols. Consequently, the investigation of the effect of tautomerism on the mechanism of the reactions of these compounds is interesting. In the present review, we attempted to combine the results of spectroscopic studies with selected data on the reactivity of five-membered heterocyclic thiols, namely, data directly concerned with the tautomeric nature of the latter. It is to be noted that there is a series of reviews and general monographs on the tautomerism itself,[1] as well as on the chemistry of certain classes of heterocyclic compounds,[2-7] which to a certain extent deal with the problems under consideration. However, new experimental data have been published recently and need to be surveyed. The new data have served as a basis for the consideration of particular types of thiols in this review.

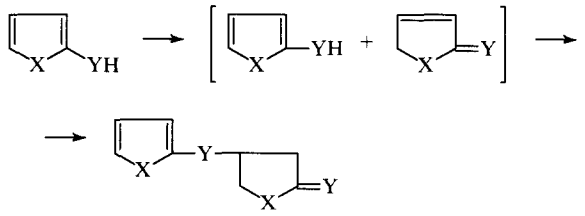
II. Furan-, thiophene- and selenophene-thiols

Unlike the hydroxy derivatives that mostly occur as oxo-forms, furan- and thiophene-thiols exist, according to all spectroscopic and other physicochemical characteristics, as mercapto-compounds.[5,6,8-12] The only report[13] that 2-mercaptoselenophene occurs in the thione form has been disproved.[14]

E D Shtefan, V Yu Vvedenskii Irkutsk Institute of Organic Chemistry, Siberian Division of the Russian Academy of Sciences, ul. Favorskogo 1, 664033 Irkutsk, Russian Federation. Fax (7-395) 246 03 31. E-mail: vlad@iochem.irkutsk.su

Received 23 June 1995
Uspekhi Khimii **65** (4) 326 – 333 (1996); translated by A V Geiderikh

At the same time, the tautomeric nature of these compounds was never doubted. Besides the thione structure of mercaptoaldimines (see the review of Litvinov et al.[15]) and the ketonic structure of the corresponding heterocyclic hydroxy derivatives (see, for example, Gronovitz's review[16]), the most important evidence for the tautomeric nature of heterocyclic thiols was the extreme lability of the thiols of the thiophene and, particularly, the furan series. The corresponding selenols are even more labile. Some of them have only recently been characterised by spectroscopic methods.[17,18] A common reason for the lability of the heterocyclic thiols and selenols proved to be associated with their tautomerism. Analysis of the auto-transformation products has shown these compounds to be dimers, which are most probably formed by the addition of the chalcogenols to their own tautomeric forms.[14,16,17-22]

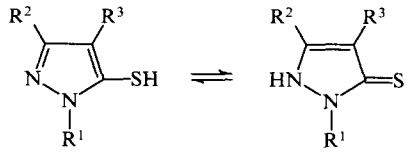


X = O, S, Se; Y = S, Se

This reaction is catalysed by triethylamine and phenylhydrazine (in the latter case, the hydrazones Y = N – NHPh of the dimeric products are formed).

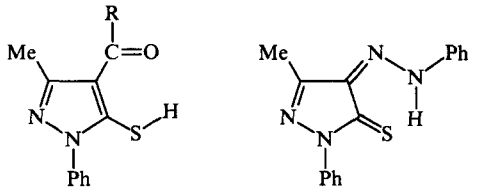
III. 5-Mercaptopyrazoles

Mercaptopyrazoles represent an unusual example of compounds where tautomerism can be detected directly by spectroscopic methods.[23]



R^1, R^2 = Me, Ph; R^3 = H, Me

The equilibrium position depends strongly on the solvent. In aprotic media, the [NH]:[SH] ratio increases with increase in the polarity of the medium. For example, the concentration of the NH-form of 5-mercapto-1,4-dimethyl-pyrazole in dioxane is close to zero, in THF it is about 5%, and in DMSO it is as high as 70%. In alcohols, the amount of the NH-form increases with increase in their ability to form hydrogen bonds. Depending on the nature of the substituent in the 4-position, intramolecular hydrogen bonds stabilise one or the other tautomer. It is the thiol form in the case of the carbonyl group, and the thione in the case of the phenylazo group.



R = H, Me, Ph

It is interesting to note that no traces of the possible third tautomer (C−H) have been found.

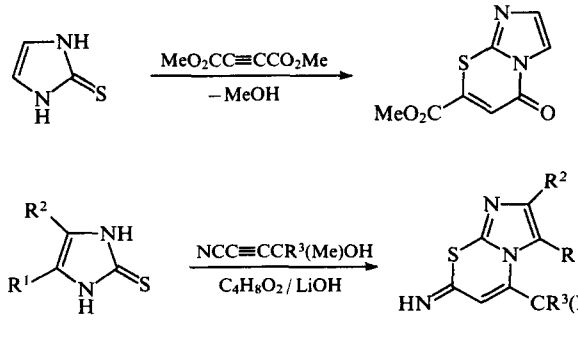
Only the SH-forms of 3-mercapto-1-methyl- and 5-mercapto-1-methyl-pyrazoles have been detected in their photoelectron spectra in nonpolar solvents.[24]

IV. Imidazolethiones and 1,3-oxazole-2-thiones

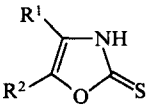
The ^{15}N NMR spectra of 2-mercapto-1-methyl-imidazole indicate that in a polar solvent (DMSO) this compound exists only in the thioamide form, while in chloroform the presence of a small amount (2%) of iminothiol form is observed.[25,26] The additional stabilisation of the thioamide form in DMSO is caused presumably by formation of hydrogen bonds with the solvent. The prevalence of the thioamide form is also corroborated by UV,[27] ^{13}C NMR,[28] and photoelectron spectroscopy,[29] quadrupole resonance,[30] and acidity constant measurements.[31] Polarographic studies have shown that 2-mercapto-1-methylimidazole occurs in the thione form in aqueous solution at pH<6, while at pH>6 it forms thiolates.[32]

The IR spectrum of 1-methylimidazole-2-thione, obtained by Ettlinger as early as 1950,[33] is identical with that of the corresponding imidazolone; this is convincing evidence in favour of the thione structure.[34] An unexpected result was obtained by Spanish investigators.[35] According to their IR and Raman spectroscopic data, in the crystalline phase imidazolethione actually exists as the pure thiol. This conclusion probably requires additional proof.

Both the sulfur and nitrogen atoms can serve as the reaction centres in the nucleophilic addition of imidazolethiones to an activated acetylenic bond.[36,37]



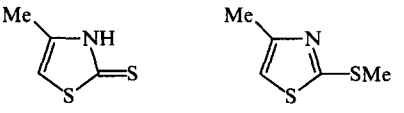
Data obtained by several investigators[29,31,38-41] have shown that the IR spectra of a series of oxazole-2-thiones provide no grounds for doubts about their thione nature.



An MNDO calculation also confirms that the thione form predominates over the thiol form. The difference between the enthalpies of formation of these two forms is 43.96 kJ mol^{-1} when $R^1 = R^2 = H$.[42]

V. Thiazole-2-thiones

The first evidence for the thione structure of thiazolethione and its methyl derivatives was obtained by Ettlinger from IR spectra which were indistinguishable from those of thiazolones.[33] These data were confirmed in later studies.[29,31,35,43-46] Sheinker, Postovskii, and Voronina supposed[43] that the thione form predominates both in the condensed phase and in solution (dioxane). This was confirmed by the comparison of the spectra of compounds **1** and **2**.



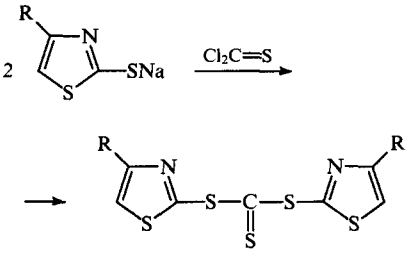
1 **2**

In addition, Flett has noted[44] that the NH vibration bands in the 3430 cm^{-1} region in the spectrum of a solid sample disappeared in a CCl_4 solution. Hence it was concluded that 4-methylthiazole-2-thione exists in the crystalline form as thioamide complexes with hydrogen bonds.

The evidence for the thione structure of 4-indolyl-2-mercaptothiazole is, firstly, the absence of SH-group absorption bands in the IR spectra, and, secondly, the presence of a maximum at 332 nm in the UV spectrum, disappearing in an alkaline medium.[45]

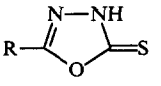
According to the MNDO calculation, the difference between the enthalpies of formation of the thione and thiol forms of the unsubstituted potential mercaptothiazole is 56.82 kJ mol^{-1}, which is evidence in favour of the thione form.[42]

In an alkaline medium, the nucleophilic centre in the mercaptothiazole molecule is the exocyclic sulfur atom. For example, sodium thiazolethiolates react with thiophosgene to give trithiocarbonates.[47]



VI. 1,3,4-Oxadiazolethiones and 1,3,4-thia(selena)diazolethiones

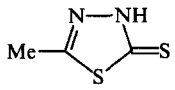
In 1956, Ainsworth obtained a series of substituted oxadiazolethiones.[48]



R = Alk, Ar, Het.

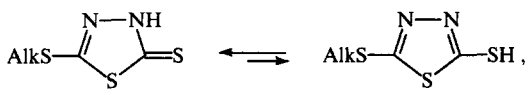
Their thione structures were confirmed by IR spectroscopic data.[48] Later studies[49,50] gave the same result.

In 1958, Ainsworth[51] found that the IR spectrum of 2-mercapto-5-phenyl-1,3,4-thiadiazole was identical with that of the corresponding oxadiazolethione; hence, this compound also exists in the thione form. A similar conclusion was also reached recently by Indian investigators[52] who studied 5-substituted 2-mercapto-1,3,4-thiadiazoles. In the ^{1}H NMR spectra of these compounds, the chemical shift (δ) of the NH proton is about 5.2–5.5 ppm. There are no SH absorption bands (2500 to 2600 cm^{-1}) in the IR spectrum of the thione **3** in the condensed state.[53]



3

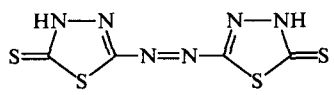
In the system



4a **4b**

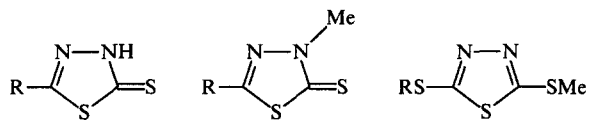
the equilibrium is significantly shifted towards the thione form, which has been confirmed by spectroscopic methods: IR (the absence of the SH-group absorption band), ^{1}H NMR [δ(NH) = 12–14 ppm], and ^{13}C NMR spectroscopy [δ(C=S) = 188 ppm].[54,55] Only in the IR spectrum of a concentrated chloroform solution, has a weak absorption of the SH group (2560 cm^{-1}) been detected, which may indicate the coexistence of two tautomeric forms.

The absorption bands corresponding to the SH group were not found in the IR spectrum of 2,2′-azo-1,3,4-thiadiazole-5-thione **5**.[56]

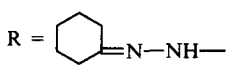


5

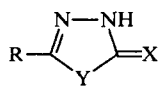
According to the data of Arvidsson and Sandström,[57] the hydrazones **6** and **7** have very similar UV spectra, differing markedly from that of the *S*-methylated compound **8**; this fact undoubtedly proves the thione structure of these compounds.

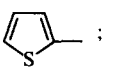


6 **7** **8**



The structures of some potential thiols and selenols of thia- and selenodiazoles were studied by ^{13}C NMR spectroscopy.[58] It was found that, on oxidation of these compounds to disulfides and diselenides respectively, the chemical shifts of the carbon atoms change significantly: the C(2) signal is shifted upfield (by about 30 ppm) and the C(5) signal is shifted downfield (by 10 ppm).

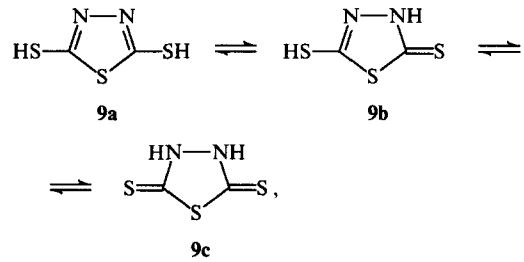


R = MeNH, *p*-MeC$_6$H$_4$NH,  ; X, Y = S, Se

Bearing in mind that disulfides and diselenides should be good models for thiol and selenol tautomerism, these data suggest that the thione and selenone structures are preferred.

VII. 5-Mercapto-1,3,4-thiadiazole-2-thiones and 1,2,4-thiadiazole-3,5-dithione

The IR spectra of 2,5-dimercapto-1,3,4-thiadiazole **9**[43]

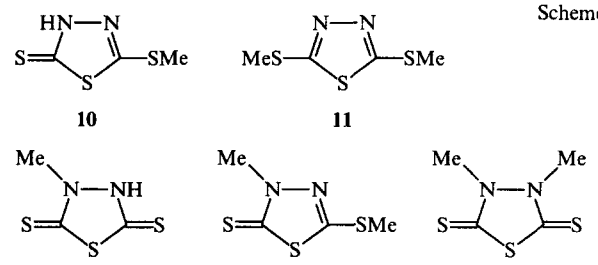


9a **9b** **9c**

contain a distinct absorption band in the region of 2489 cm^{-1} (corresponding to the SH group) and intense bands in the range 2860–3067 cm^{-1}, indicating the presence of the NH group. Hence it was concluded that compound **9** has a mixed thione-thiol structure, i.e. form **9b** predominates.

Later, Thorn[59] undertook a detailed study of the absorption spectra of compound **9** and a series of its methyl derivatives **10**–**14** (Scheme 1).

Scheme 1



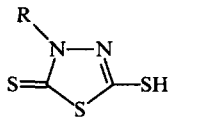
10 **11** **12** **13** **14**

Compound	**9**	**10**	**11**	**12**	**13**	**14**
λ_{max} /nm	335	318	288	333	320	324
	260	235	–	260	243	268

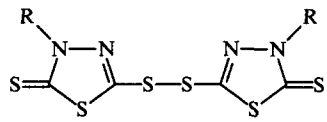
Analysis of the UV spectra revealed a striking similarity of the absorption maxima of compounds **9**, **12**, and **14** that appeared to show unambiguously that they have the dithione structure. However, this conclusion was not confirmed by IR spectra. In all the spectra except that of compound **11**, there is a band at 1475–1508 cm^{-1}, which has been assigned to the thioamide fragment. However, for all the compounds except compound **14**, the band at 1415–1435 cm^{-1}, which should be assigned to the iminothiol group, is also detected. Furthermore, in the spectra of compounds **9** and **12** bands in the thiol region (2590 cm^{-1} and 2555 cm^{-1} respectively) were detected. To account for this discrepancy between the IR and UV spectroscopic data, Thorn assumed[59] that compounds **9** and **12** exist in a mixed form in a concentrated chloroform solution (i.e. under the conditions of the recording of the IR spectra) while the dithione form prevails in dilute alcoholic solution used for UV spectroscopy. Stanovnik and Tišler[60] suggested a 'monomercapto-monodipolar' structure for compound **9**. Later, the presence of at least one thiol group was established[61] by IR spectroscopy, this group being deprotonated on formation of complexes with metals.

Zaidi et al.[62] have noted the presence of a 'weak' absorption band (at about 2490 cm^{-1}) due to the thiol group, in contrast to the 'medium' bands at 3060 cm^{-1} and 2875 cm^{-1} corresponding to the N–H bond. They suggested that structure **9b** should be discounted, because the band due to the SH group is too weak compared with that of the NH group; thus, 2,5-dimercapto-1,3,4-thiadiazole exists mainly in the dithione form, which is in equilibrium with a small amount of the thiol form. However, in the next paper[63] a modified view was expressed: here the SH

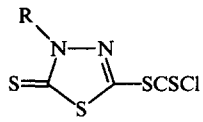
bands were classified as 'medium', and the NH bands — as 'strong'. This has two possible explanations. Firstly, the authors[63] may have been influenced by their own results on the structures of complexes of compound **9** with transition metals, where the ligand is in the thione-thiolate form **9b**. Secondly, the important study by Anthony et al.[64] was published a year earlier. They used for the first time ^{13}C NMR spectroscopy of chloroform solutions in order to solve this problem. The chemical shifts of the two carbon atoms in the rings of compounds **15** – **17** were found to differ significantly (186 – 188 ppm and 144 – 154 ppm), while in the symmetrical dithione **14** the shift is 180 ppm. This fact proves reliably the presence of structure **9b**. In the IR spectra of compound **15**, bands at 2560 cm^{-1} and 930 – 933 cm^{-1} were detected, disappearing on its oxidation with iodine to the disulfide **16**. They were assigned to S – H stretching and C – S – H deformation vibrations.



15



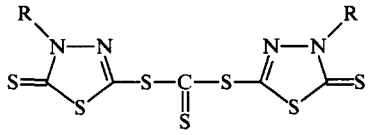
16



17

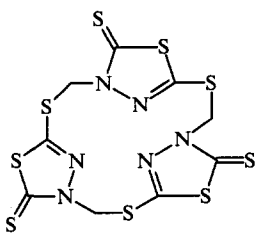
R = Ph, Me

Mercaptothiones do not yield N-adducts in the reaction with thiophosgene, but form trithiocarbonates.[47,64]

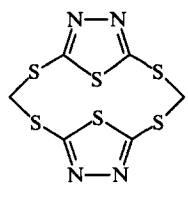


R = Me, Ar

Unsubstituted mercaptothiadiazolethione reacts with dibromoalkanes in the presence of bases to form various macroheterocyclic compounds.[65] The final product composition depends strongly on the reaction conditions and the selection of the initial reactants. For example, by using dibromomethane with one equivalent of alkali (KOH), it is possible to obtain trithiathiadiazolinophanetrithione **18**, i.e. the product of the reaction at both S and N atoms. With two equivalents of alkali, tetrathiathiadiazolophane **19** can be produced.

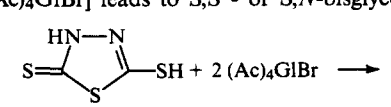


18

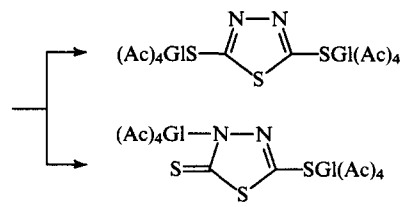


19

Depending on the conditions, the reaction with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide [α-acetobromoglucose, $(Ac)_4GlBr$] leads to *S,S'*- or *S,N*-bisglycosides.[66]

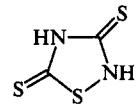


20



The *S,N*-adduct is formed either *via* the stepwise glycosidation of compound **20** by one and then by another mole of $(Ac)_4GlBr$, or by the glycosidation of the mercury salt of **20**, or by the trans-glycosidation of the *S,S'*-adduct in the presence of $HgBr_2$.

In the case of 1,2,4-thiadiazole-3,5-dithione, the IR spectroscopic data seem to be in favour of the dithione structure.[67]



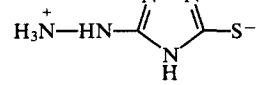
The intense absorption at 3010 cm^{-1} and 2830 cm^{-1} is due to the NH group, while the SH band in the 2600 cm^{-1} region is absent.

VIII. 1,2,4-Triazolethiones

In 1959, Reynolds and VanAllan[68] compared the UV spectra of potential mercaptotriazoles and their *S*-methyl and *S*-acyl-derivatives and concluded that the thione form predominates. This conclusion was confirmed[29, 69-71] by means of the IR and NMR spectroscopy of 3-mercapto-1,2,4-triazoles having various substituents in the 4- and 5-positions. In the IR spectrum of 4-amino-1,2,4-triazole-3,5-dithione, SH bands are absent, but there are bands at 1333 cm^{-1} and 1519 cm^{-1}, which can be assigned to the C=S and HN – C=S fragments respectively. The latter two bands disappear on alkylation of the dithione with methyl iodide.[72] According to X-ray diffraction data,[73] 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole crystallises in the thione form.

At the same time, the IR and ^1H NMR spectra of 5-ferrocenyl-4-phenyl-1,2,4-triazole-3-thiol indicate that it is more likely to exist as a mixture of tautomers.[74] The same conclusion has been made for 4-amino-5-mercaptotriazoles and the Schiff's bases derived from them. In the IR spectra of these compounds, there is a weak absorption in the 2480 – 2550 cm^{-1} region, which can be assigned to the thiol group. In addition, the thiol proton with a chemical shift of about 8.5 – 8.8 ppm was detected in the ^1H NMR spectra, together with the NH-group protons.[75,76] Furthermore, the bold hypothesis has been put forward[77] that the absence of signals in the thiol region of the IR spectra of 4-amino-5-mercaptotriazoles does not necessarily indicate the absence of the thiol form, since the S – H bond usually has a very weak absorption.

A zwitter-ionic structure has been proposed for 3-hydrazino-5-mercapto-1,2,4-triazole on the basis of crystallographic data.[78]

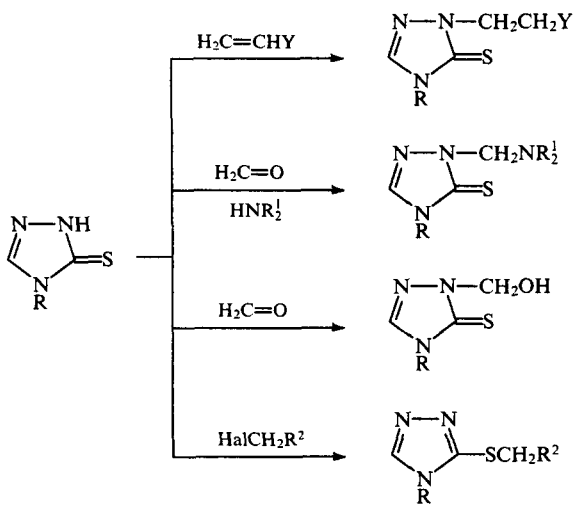


Thus, the C – S bond length is 0.174 nm, which is, of course, closer to that of the single bond and not the double bond.

In 1,2,4-triazolethiones, both the sulfur and nitrogen atoms can act as nucleophilic centres, depending on the nature of the attacking reagent and on the reaction conditions (Scheme 2).[79-83]

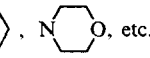
The introduction of an arylamino group into the 5-position does not change the mode of nucleophilic substitution reactions.[84]

Scheme 2



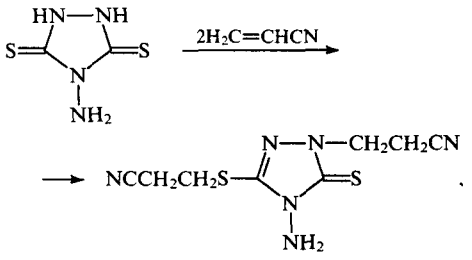
R = *p*-XC_6H_4, X = H, Cl, OEt;

Y = CN, α-Py;

NR^1_2 = , etc.;

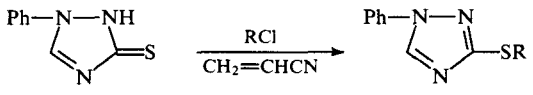
R^2 = H, Ph, $C_6H_4NO_2$-*p*, $CONH_2$, COOH, CH_2COOH

Regardless of the nature of the substituents in the 4- and 5-positions, cyanoethylation occurs at the nitrogen atom [72,85-87] with one exception:[72]

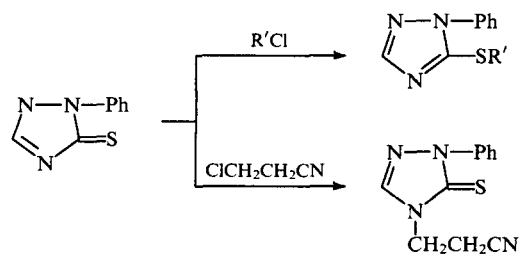


On the other hand, compounds of the $HalCH_2R$ type usually react at the sulfur atom.[79,81-85,87-89]

The situation is changed if the aryl substituent is present in the 1- or 2-position. In the case of 1-phenyl-1,2,4-triazole-3-thione, cyanoethylation at the sulfur atom takes place, while alkylation of 2-phenyl-1,2,4-triazole-3-thione by β-chloropropionitrile can occur at a nitrogen atom.[90]



R = CH_2CH_2CN, CH_2CH_2COOH, CH_2Ph

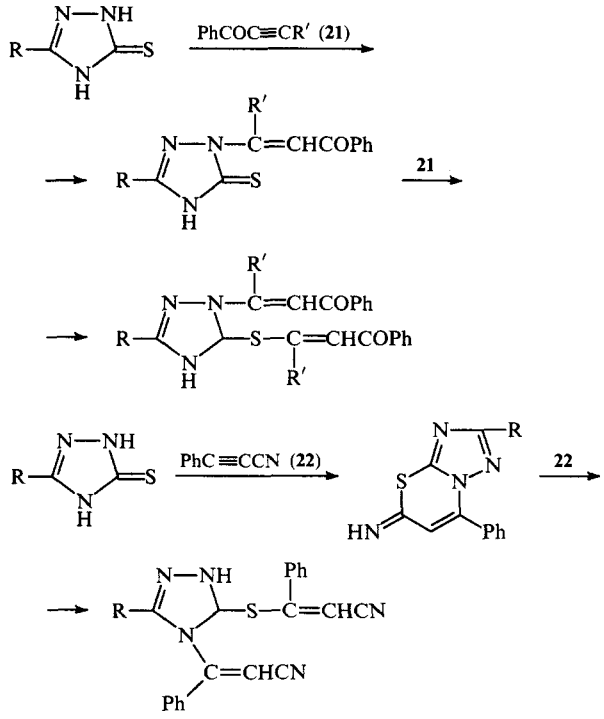


R′ = CH_2CH_2COOH, CH_2Ph

The mechanism of the cyanoethylation reaction is believed to begin (in all cases) with the attack of the reagent on the sulfur atom, since it carries a greater negative charge. However, this is followed by transcyanoethylation with the participation of a second reagent molecule. This is based on quantum-chemical calculations of the charge distribution in the triazolethione molecules by Hückel's MO method.[90]

The acylation of 4,5-disubstituted triazole-3-thiones with benzoyl and cinnamoyl chlorides yields ultimately C–N-products; however, when phenyl substituents are present in both positions and the reaction is carried out in an alkaline medium, it is possible to isolate C–S-derivatives, which are, however, readily transacylated on heating.[86,87]

Under ethyne pressure in the presence of alkali, 1,2,4-triazolethiones give *S*-vinyl derivatives. Further vinylation at the nitrogen is possible when catalysts (cuprous chloride, cadmium acetate) are used.[91-93] The formation of divinylation products also occurs in the case of various substituted ethynes.[94,95]

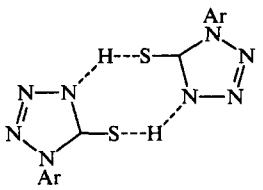


However, initial *N*-vinylation takes place in this case.

IX. Tetrazolethiones

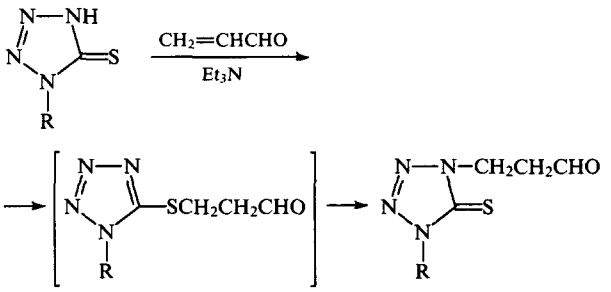
In 1958, Lieber et al.[96] reported the absence of bands corresponding to SH groups in the IR spectra of aryltetrazolethiones. The absorptions in the 1470–1500 cm^{-1} and 1338–1359 cm^{-1} regions were assigned to the N–C=S and C=S fragments respectively. The UV spectra of methyl- and benzyl-thiotetrazoles differed from those of mercapto-derivatives, resembling more closely the spectra of non-tautomeric tetrazoles,[97] which also constituted evidence in favour of the thione structure.

Kauer and Sheppard concluded that the UV and IR spectra of arylmercaptotetrazoles did not correspond to those of aryltetrazole systems.[98] However, the question of the position of the proton remained unsolved, and it was suggested that arylmercaptotetrazoles may exist (at least in the solid state or in weakly polar solvents) as hydrogen-bonded dimers.

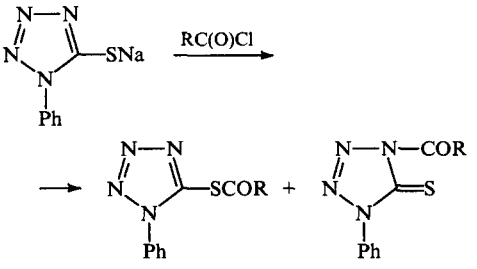


Fairly definite results have been obtained by means of ^{13}C NMR spectroscopy.[29,58,99-101] The chemical shift of the carbon atom in substituted tetrazolethiones was shown to be 163-165 ppm (depending on the substituent and the solvent), while in the *S*-derivatives (sulfides, disulfides, etc.) this value is lower by 8-18 ppm. Thus, the thione structure of the compounds under consideration is confirmed. According to ^{15}N NMR spectra,[102] most tetrazolethiones have the 2H-structure; however, Stefaniak[103] believes 4*H*-tetrazole-5-thione to be the dominant structure.

From the chemical viewpoint, the properties of tetrazolethiones are similar to those of triazolethiones. For example, they undergo pyridylethylation[80] and aminomethylation[104] at the nitrogen atom adjacent to the thione group. At the same time, tetrazolethiones are more prone to form sulfides than triazolethiones in reactions with α,β-unsaturated carbonyl compounds and in the cyanoethylation reaction.[99,105,106] Addition occurs at the nitrogen atom in presence of triethylamine and at the sulfur atom in an alkaline medium. The sulfides formed can rearrange into C-N-adducts. Moreover, a special experiment involving the use of ^1H NMR spectroscopy showed the C-S-adduct to be the intermediate in the reaction catalysed by triethylamine.

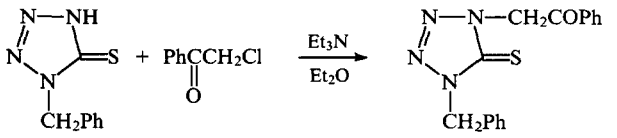


The mode of acylation depends on both the nature of the substituent in the ring and on the acyl halide structure.[100,107,108] For example, sodium 1-phenyltetrazole-5-thiolate gives a mixture of products of the acylation at the sulfur atom and the nitrogen atom in the 4-position, the fraction of the latter decreasing with increase in the bulk of the substituent R.

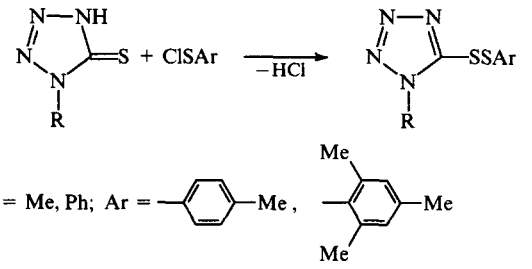


23 **24**

The yields of compounds **23** and **24** are equal for R = Me, while for R = Bu^t the C-N-adduct is not formed. In 1-alkyltetrazolethiones not only the nitrogen atom at the 4-position but also the nitrogen atom at the 2-position undergoes acylation, and a mixture of three products is formed. Arenesulfonyl chlorides, benzoyl chloride, and compounds containing the Hal-C(sp^3) bond react at the sulfur atom. Only one exception is known.



Arylsulfanyl chlorides react with tetrazolethiones in ether in the presence of pyridine to give disulfides.[109]



Diazomethane reacts with 1-methyltetrazole-5-thione to give a mixture of *S*-methyl- and 4-*N*-methyl-derivatives,[101] while oxiranes give spirocyclic 1,3-oxathiolanes.[110]

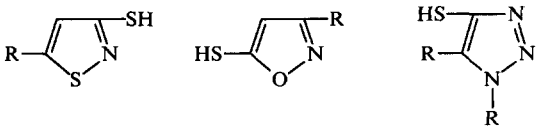


The thione structure was assigned[111] to 1,2,3,4-tetrazole-5-thione on the basis of the absence of absorption at 2500-2600 cm^{-1} in the IR spectrum.

In alkaline medium, this compound is alkylated and acylated at the sulfur atom.[100,111-113]

* * *

Comparative analysis of the structures of tautomeric five-membered heterocyclic thiols leads to the following conclusions. The thione form predominates in all azoles having the mercapto-group between two heteroatoms, as happens, for instance, in imidazole-2-thione, thiadiazole-2-thione, and tetrazolethione. 5-Mercaptothiadiazole-2-thione is an exception; it contains a thiol group, unlike, for example, 1,2,4-thiadiazole-3,5-dithione. On the other hand, if the above condition is not fulfilled and at least one of the 'neighbours' of the mercapto group is a carbon atom, the predominance of the thiol form may be expected. Among such compounds are furan-, thiophene-, and selenophene-thiols, mercaptopyrazoles, as well as 3-mercaptoisothiazoles **25**, 5-mercaptoisoxazoles **26**, and 4-mercapto-1,2,3-triazoles **27**, which have not been considered here (see the review of Elguero et al.[1]).



25 **26** **27**

As to the characteristic features of the chemical properties of the compounds considered, one may note that the predominance of one or another tautomeric form does not often determine the regioselectivity of the reaction. The alkylation of azolethiones with alkyl halides at the sulfur atom and the autothiylation of furan-, thiophene-, and selenophene-thiols may be given as examples.

References

1. J Elguero, C Marzin, A R Katritzky, P Linda *The Tautomerism of Heterocyclic Compounds* (New York: Academic Press, 1976)
2. J Sandström *Adv. Heterocycl. Chem.* **9** 165 (1968)
3. A R Katritzky, J M Lagowsky *Adv. Heterocycl. Chem* **2** 3 (1963)
4. F Kurzer *Adv. Heterocycl. Chem.* **5** 119 (1965)
5. S Gronowitz, A-B Hörnfeldt, in *Thiophene and Its Derivatives* (New York: Interscience, 1986) p. 136
6. M V Ul'ev, E D Shtefan, V Yu Vvedenskii *Usp. Khim.* **60** 2528 (1991) [*Russ. Chem. Rev.* **60** 1309 (1991)]
7. B V Trzhtsinskaya, N A Abramova *Sulfur Rep.* **10** 389 (1991)
8. E Niwa, H Aoki, H Tanaka, K Munakata, M Namiki *Chem. Ber.* **99** 3215 (1966)
9. A V Anisimov, V S Babaitsev, E A Viktorova *Khim. Geterotsikl. Soedin.* 1313 (1980)
10. J J Peron, P Saumagne, J M Lebas *Spectrochim. Acta, Part A* **26** 1651 (1970)
11. H Lumbroso, D M Bertin, P Cagniant *Bull. Soc. Chim. Fr.* 1720 (1970)
12. B Cederlund, R Lantz, A-B Hörnfeldt, O Thorstad, K Undheim *Acta Chem. Scand. Ser. B* **31** 198 (1977)
13. J Morel, C Paulmier, D Semard, P Pastour *Bull. Soc. Chim. Fr.* 3547 (1971)
14. V Yu Vvedenskii, E D Shtefan, R N Malyushenko, E N Deryagina *Khim. Geterotsikl. Soedin.* (1996) (in the press)
15. V P Litvinov, A F Vaisburg, V Yu Mortikov *Sulfur Rep.* **11** 321 (1992)
16. S Gronowitz *Khim. Geterotsikl. Soedin.* 1445 (1994)
17. V Yu Vvedenskii, S V Zinchenko, E D Shtefan, M V Ulyev, A R Zhnikin, T A Shkarupa, E N Deryagina *Sulfur Lett.* **14** 129 (1992)
18. V Yu Vvedenskii, E D Shtefan, R N Malyushenko, E N Deryagina *Khim. Geterotsikl. Soedin.* 891 (1994)
19. V Yu Vvedenskii, S V Zinchenko, T A Shkarupa, N A Korchevin, E N Deryagina, M G Voronkov *Dokl. Akad. Nauk SSSR* **305** 624 (1989)
20. G S Ponticello, C N Habecker, S L Varga, S M Pitzenberger *J. Org. Chem.* **54** 3223 (1989)
21. V Yu Vvedenskii, E D Shtefan, M V Ulyev, E N Deryagina, M G Voronkov *Sulfur Lett.* **17** 257 (1994)
22. V Yu Vvedenskii, T A Shkarupa, S V Zinchenko, A R Zhnikin, E N Deryagina, M G Voronkov *Zh. Org. Khim.* **26** 2237 (1990)
23. A Maquestiau, Y Van Haverbeke, J-C Vanoververlt *Bull. Soc. Chim. Belg.* **86** 949 (1977)
24. C Guimon, G Pfister-Guillouzo, M Begtrup *Can. J. Chem.* **61** 1197 (1983)
25. E Bojarska-Olejnik, L Stefaniak, M Witanowski, B T Hamdi, G A Webb *Magn. Reson. Chem.* **23** 166 (1985)
26. R S Balestrero, D M Forkey, J G Russell *Magn. Reson. Chem.* **24** 651 (1986)
27. P Bouin-Roubaud, J Kister, M Rajzmann, L Bouscasse *Can. J. Chem.* **59** 2883 (1981)
28. E Bojarska-Olejnik, L Stefaniak, M Witanowski, G A Webb *Bull. Pol. Acad. Sci., Chem.* **34** 295 (1986)
29. C Guimon, G Pfister-Guillouzo *Tetrahedron* **30** 3831 (1974)
30. M L S Garsia, J A S Smith, P M G Bavin, C R Ganellin *J. Chem. Soc., Perkin Trans. 2* 1391 (1983)
31. G Kjellin, J Sandström *Acta Chem. Scand.* **23** 2888 (1969)
32. Z Fijalek, P Zuman *Anal. Lett.* **23** 1213 (1990)
33. M Ettlinger *J. Am. Chem. Soc.* **72** 4699 (1950)
34. P Karagiannidis, P Aslanidis, S Papastefanou *Polyhedron* **9** 981 (1990)
35. J Perez-Peña, M Gonzalez-Davila, M Suarez-Tangil, J Hernandez-Brito *Collect. Czech. Chem. Commun.* **54** 2045 (1989)
36. R M Acheson, J D Wallis *J. Chem. Soc., Perkin Trans. 1* 415 (1981)
37. USSR P. 1 121 265; *Byull. Izobret.* (40) 65 (1984); *Chem. Abstr.* **102** 203 978 (1985)
38. J F Willems, A Vandenberghe *Bull. Soc. Chim. Belg.* **70** 745 (1961)
39. R Gompper, H Herlinger *Chem. Ber.* **89** 2816 (1956)
40. R Gompper, H Herlinger *Chem. Ber.* **89** 2825 (1956)
41. F Weygand, H J Bestmann, F Steden *Chem. Ber.* **91** 2537 (1958)
42. G S Kapsomenos, P P Akrivos *Can. J. Chem.* **66** 2835 (1988)
43. Yu N Sheinker, I Ya Postovskii, N M Voronina *Zh. Fiz. Khim.* **33** 302 (1959)
44. M St C Flett *J. Chem. Soc.* 347 (1953)
45. Yu I Smushkevich, Ts M Babueva, N N Suvorov *Khim. Geterotsikl. Soedin.* 91 (1969)
46. W O Foye, N Abood, J M Kauffman, Y-H Kim, B R Patel *Phosphorus Sulfur* **8** 205 (1980)
47. F Runge, Z El-Hewehi, E Taeger *J. Prakt. Chem.* **18** 262 (1962)
48. C Ainsworth *J. Am. Chem. Soc.* **78** 4475 (1956)
49. W R Sherman *J. Org. Chem.* **26** 88 (1961)
50. S Misra, B L Dubey, S C Bahel *Synth. React. Inorg. Metal.-Org. Chem.* **24** 1027 (1994)
51. C Ainsworth *J. Am. Chem. Soc.* **78** 5201 (1958)
52. S Misra, B L Dubey, S C Bahel *Synth. React. Inorg. Metal.-Org. Chem.* **21** 637 (1991)
53. A C Fabretti, G C Franchini, G Peyronel *Spectrochim. Acta, Part A* **36** 517 (1980)
54. P Umapathy, A R Budhkar *Synth. React. Inorg. Metal.- Org. Chem.* **16** 1289 (1986)
55. A R Katritzky, Z Wang, R J Offerman *J. Heterocycl. Chem.* **27** 139 (1990)
56. N Petri, O Glemser *Chem. Ber.* **94** 553 (1961)
57. K Arvidsson, J Sandström *Acta Chem. Scand.* **15** 1179 (1961)
58. J R Bartels-Keith, M T Burgess, J M Stevenson *J. Org. Chem.* **42** 3725 (1977)
59. G D Thorn *Can. J. Chem.* **38** 1439 (1960)
60. B Stanovnik, H Tišler *Croat. Chem. Acta.* **37** 17 (1965); *Chem. Abstr.* **63** 2967b (1965)
61. M R Gajendragad, U Agarwala *Aust. J. Chem.* **28** 763 (1975)
62. S A A Zaidi, D K Varshney *J. Inorg. Nucl. Chem.* **37** 1804 (1975)
63. S A A Zaidi, D K Varshney *J. Inorg. Nucl. Chem.* **39** 581 (1977)
64. U Anthony, B M Dahl, H Eggert, C Larsen, P H Nielsen *Acta Chem. Scand., Ser. B* **30** 71 (1976)
65. S Pappalardo, F Bottino, C Tringali *J. Org. Chem.* **52** 405 (1987)
66. G Wagner, B Dietzsch *J. Prakt. Chem.* **315** 915 (1973)
67. H J Emeleus, A Haas, N Sheppard *J. Chem. Soc.* 3168 (1963)
68. G A Reynolds, J A VanAllan *J. Org. Chem.* **24** 1478 (1959)
69. F Malbec, R Milcent, G Barbier *J. Heterocycl. Chem.* **21** 1689 (1984)
70. V I Kelarev, G A Shvekhgeimer, A F Lunin *Khim. Geterotsikl. Soedin.* 1271 (1984)
71. S Gopinathan, S A Pardhy, A P Budhkar, C Gopinathan *Synth. React. Inorg. Metal.-Org. Chem.* **18** 823 (1988)
72. A D Sinegibskaya, E G Kovalev, I Ya Postovskii *Khim. Geterotsikl. Soedin.* 562 (1973)
73. R G Dickinson, N W Jacobsen *Anal. Chem.* **41** 1324 (1969)
74. W Hui, Z Yulan, H Youhong, W Shaozu *Synth. React. Inorg. Metal.-Org. Chem.* **24** 1121 (1994)
75. K Chaturvedi, O P Pandey, S K Sengupta *Synth. React. Inorg. Metal.-Org. Chem.* **24** 1487 (1994)
76. S Goel, O P Pandey, S K Sengupta *Bull. Soc. Chim. Fr.* 771 (1989)
77. B S Garg, P C Gupta, S K Garg *Synth. React. Inorg. Metal.-Org. Chem.* **18** 643 (1988)
78. M E Senko, D H Templeton *Acta Crystallogr.* **11** 808 (1958)
79. I L Shegal, I Ya Postovskii *Khim. Geterotsikl. Soedin.* 133 (1965)
80. I Ya Postovskii, V L Nirenburg *Khim. Geterotsikl. Soedin.* 161 (1965)
81. I Ya Postovskii, I L Shegal *Khim. Geterotsikl. Soedin.* 443 (1965)
82. I L Shegal, I Ya Postovskii *Khim. Geterotsikl. Soedin.* 449 (1965)
83. I Ya Postovskii, I L Shegal *Khim. Geterotsikl. Soedin.* 443 (1966)
84. R G Dubenko, I M Bazavova, P S Pel'kis *Khim. Geterotsikl. Soedin.* 129 (1971)
85. M M Tsitsika, S M Khripak, I V Smolanka *Khim. Geterotsikl. Soedin.* 1425 (1974)
86. M M Tsitsika, S M Khripak, I V Smolanka *Khim. Geterotsikl. Soedin.* 851 (1974)
87. M M Tsitsika, S M Khripak, I V Smolanka *Khim. Geterotsikl. Soedin.* 844 (1975)
88. H M Eisa *Sulfur Lett.* **10** 239 (1990)
89. A A Hassan, N K Mohamed, Yu R Ibrahim, K U Sadek, A-F E Mourad *Bull. Chem. Soc. Jpn.* **66** 2612 (1993)
90. E G Kovalev, I Ya Postovskii *Khim. Geterotsikl. Soedin.* 1138 (1970)
91. G G Skvortsova, B V Trzhtsinskaya, L F Teterina, V K Voronov, M N Popova *Khim. Geterotsikl. Soedin.* 1561 (1977)
92. B V Trzhtsinskaya, G G Skvortsova, Yu A Mansurov, P I Buchin, M G Viderker *Khim.-Farm. Zh.* **16** 1466 (1982)

93. B V Trzhtsinskaya, E V Rudakova, A V Afonin, B Z Pertsikov, Yu A Mansurov, V P Aksenov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1674 (1986)
94. L I Vereshchagin, R L Bol'shedvorskaya, G A Pavlova, N V Alekseeva *Khim. Geterotsikl. Soedin.* 1552 (1979)
95. N D Abramova, B V Trzhtsinskaya, Yu M Skvortsov, A G Mal'kina, A I Albanov, G G Skvortsova *Khim. Geterotsikl. Soedin.* 1051 (1982)
96. E Lieber, C N R Rao, C N Pillai, J Ramachandran, R D Hites *Can. J. Chem.* **36** 801 (1958)
97. E Lieber, J Ramachandran, C N R Rao, C N Pillai *Can. J. Chem.* **37** 563 (1959)
98. J C Kauer, W A Sheppard *J. Org. Chem.* 3580 (1967)
99. G L'Abbe, G Vermeulen, J Flemal, S Toppet *J. Org. Chem.* **41** 1875 (1976)
100. G L'Abbe, S Toppet, G Verhelst, C Martens *J. Org. Chem.* **39** 3770 (1974)
101. M Narisada, Y Terui, M Yamakawa, F Watanabe, M Ohtani, M Miyazaki *J. Org. Chem.* **50** 2794 (1985)
102. E Bojarska-Olejnik, L Stefanyak, M Witanowski, G A Webb *Bull. Chem. Soc. Jpn.* **59** 3263 (1986)
103. L Stefaniak, Private communication
104. I Ya Postovskii, V L Nirenburg *Zh. Obshch. Khim.* **34** 2517 (1964)
105. I Ya Postovskii, V L Nirenburg *Zh. Obshch. Khim.* **34** 3200 (1964)
106. E Lippmann, D Reifegerste *Z. Chem.* **15** 146 (1975)
107. E Lippmann, D Reifegerste, E Kleinpeter *Z. Chem.* **13** 134 (1973)
108. E Lippmann, D Reifegerste, E Kleinpeter *Z. Chem.* **14** 16 (1974)
109. G Stajer, E A Szabo, J Pintye, F Klivenyi, P Sohar *Chem. Ber.* **107** 299 (1974)
110. P-C Tromm, H Heimgartner *Helv. Chim. Acta* **73** 2287 (1990)
111. E Lieber, C N Pillai, J Ramachandran, R D Hites *J. Org. Chem.* **22** 1750 (1957)
112. C Christophersen, A Holm *Acta Chem. Scand.* **25** 2015 (1971)
113. E Lieber, E Oftedahl, C N R Rao *J. Org. Chem.* **28** 194 (1963)