1,2,3-Dithiazole chemistry in heterocyclic synthesis

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Abstract

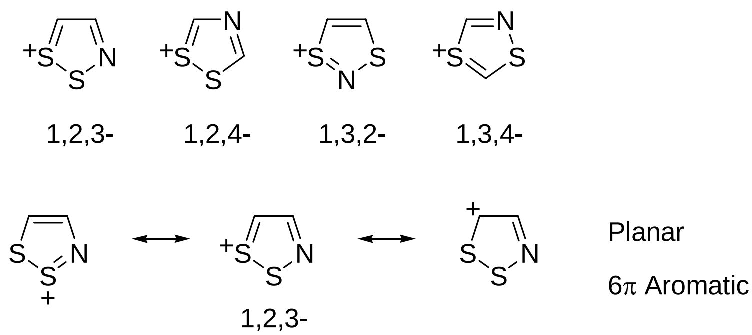
The chemistry of various 5*H*-1,2,3-dithiazoles is investigated with emphasis on assisted ring opening and ring closure reactions leading to new heterocycles. Thus on treatment with catalytic tetraalkylammonium iodide *N*-(2-chloropyrid-3-yl)- and *N*-(4-chloropyrid-3-yl)-4-chloro-1,2,3-dithiazol-5*H*-imines **19** and **20** give thiazolo[5,4-*b*]pyridine-2-carbonitrile **16** and thiazolo-[4,5-*c*]pyridine-2-carbonitrile **17** respectively. Similar treatment of bisdithiazoles **29** and **30** afford high yielding routes to 1,3,4-thiadiazole-2,5-dicarbonitrile **31** and thiazole-2,4,5-tricarbonitrile **32** respectively. *N*-(Pyrid-3-yl)-4-chloro-1,2,3-dithiazol-5*H*-imine **36** reacts with secondary alkylamines to give as main product pyrido[2,3-*d*]pyrimidines **37** and several minor byproducts including a deep green quinoidal 2,2'-bithiazole **40**. Dithiazolylidenacetonitriles **43** react with either anhydrous HBr or tetraalkylammonium chloride to afford a series of 3-halo-4-substituted-isothiazole-5-carbonitriles **45** and **52** respectively. The reactions of dithiazoles **43** with tetraalkylammonium chloride are complicated owing to the formation of isothiazolo-pentathiepin-8-carbonitrile **53**, isothiazolodithiin-4,5,7-tricarbonitrile **54**, tetracyanothiophene **56** and an unidentified compound **55** whose possible structures are proposed. The mechanistic rationales for the formation of the identified products are proposed.

Keywords: Heterocycle, dithiazole, isothiazole, thiazole, acetylene

Contents

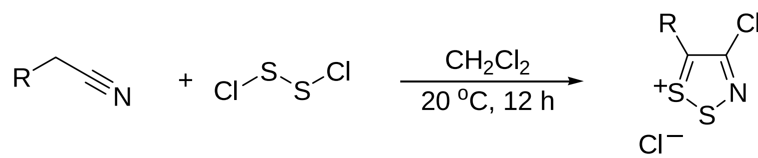
Introduction

1,2,3-Dithiazole is one of the four possible dithiazole systems all of which are reported in the literature as cations. The salts are planar, 6π and therefore aromatic and can be adequately represented by three canonical forms where the charge (identifying the three most electrophilic sites) is distributed at C-5 or on either of the ring sulfur atoms (Scheme 1).



Scheme 1

1,2,3-Dithiazolium salts are commonly prepared from substituted acetonitrile derivatives to afford the 5-substituted-4-chloro-1,2,3-dithiazolium chlorides **1**.[1,2] One example has appeared in the literature where phenylacetoxime was treated with disulfur dichloride to afford the 5-chloro-4-phenyl-1,2,3-dithiazolium chloride **2** and development of this route could provide access to 5-chloro-4-substituted-1,2,3-dithiazolium salts.[3,4]



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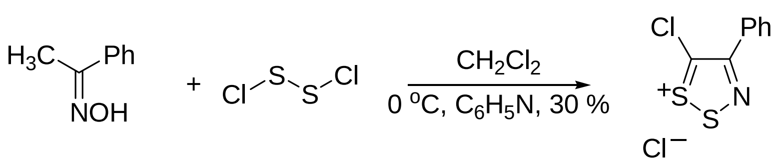
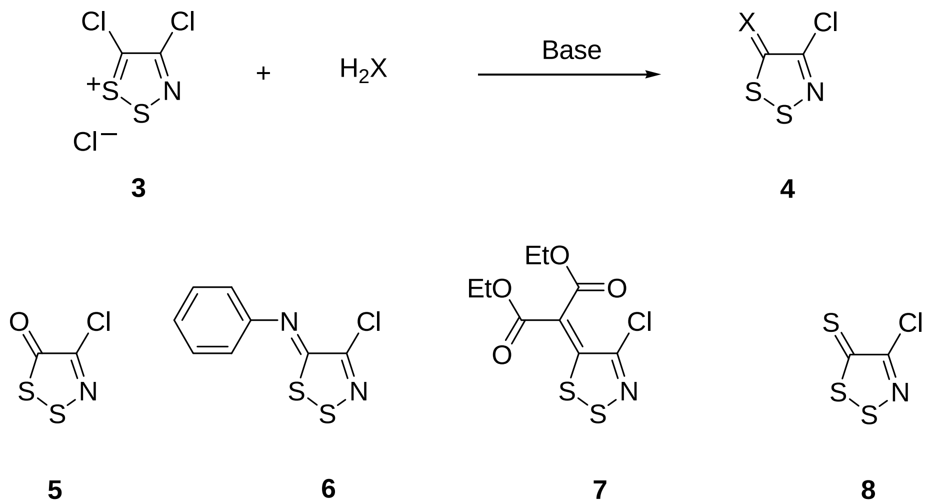


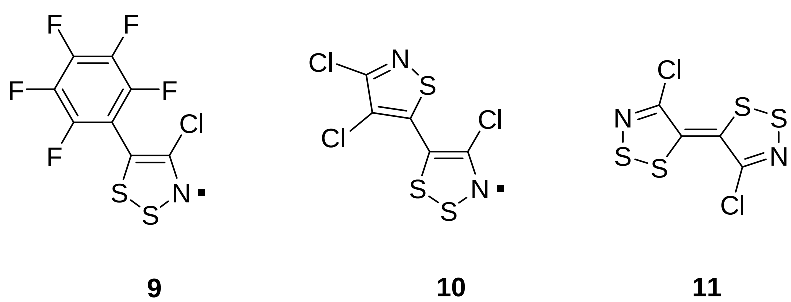
2

Our interest focuses on the chemistry of the readily available 4,5-dichloro-1,2,3-dithiazolium chloride **3** prepared from chloroacetonitrile and disulfur dichloride.[5] Dithiazolium chloride **3** on treatment with nucleophilic species affords neutral 5*H*-dithiazoles **4** (*eg*. treatment of dithiazolium **3** with H_2O, aniline, diethyl malonate or H_2S provides 1,2,3-dithiazolone **5**, dithiazolimine **6**, dithiazolylidene **7** and dithiazolethione **8** respectively in good yields (Scheme 2).[5]

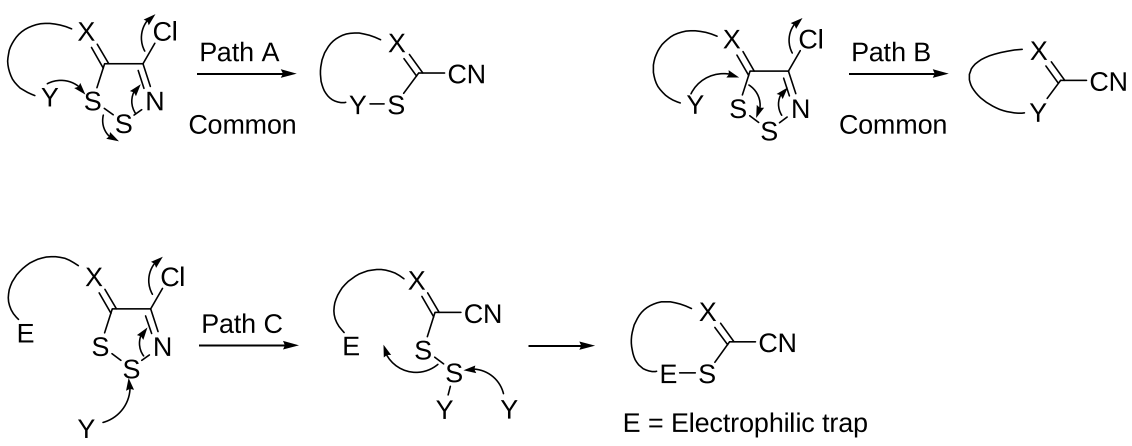


Scheme 2

1,2,3-Dithiazoles have uses in both biological and material sciences: *N*-aryl-dithiazolimines show interesting antifungal,[6] antibacterial,[7] and herbicidal[8] activities. A search for organic conductors based on neutral radicals has led to the preparation of two 1,2,3-dithiazolyl radicals **9**[1] and **10**[9] and also a tetrathiadiazafulvalene analogue **11**[10] has been prepared and studied.



Our interest in 1,2,3-dithiazole chemistry revolves around the construction of dithiazole systems that can be converted into new heterocyclic systems *via* ring transformation. The majority of these ring transformations involve the initial preparation of a neutral dithiazole which supports a potentially nucleophilic side chain or substituent capable of attacking the electrophilic dithiazole at either S-1 (Path A) or at C-5 (Path B) with subsequent ring opening. Dithiazoles, however, can also be ring opened with the use of soft nucleophiles to afford the disulfide intermediate **12** (Path C) (Scheme 3). This disulfide can be a source of both electrophilic and nucleophilic sulfur.



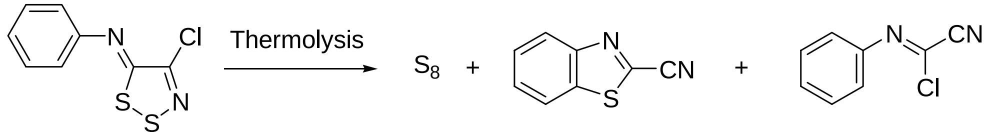
12

Scheme 3

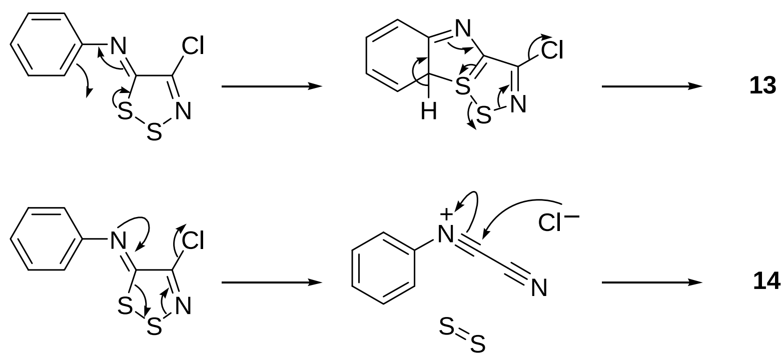
Various dithiazolylidenes have been prepared specifically with these mechanistic possibilities in mind in order to broaden the capability of dithiazolium chloride **3** as a useful synthetic tool. Emphasis will be made on the *in situ* generation of disulfides **12** endowed with electrophilic traps for nucleophilic sulfur (Path C).

1. Synthesis of thiazolopyridine-2-carbonitriles

Benzo[*d*]thiazole-2-carbonitrile **13** can be prepared readily from the thermolysis of *N*-phenyl-1,2,3-dithiazol-5*H*-imine **6** in particular where the aryl substituent is electron rich.



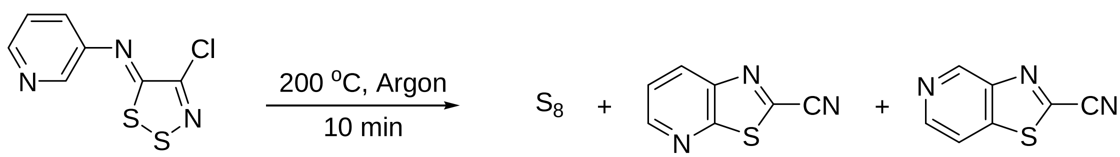
6 **13** **14**



Scheme 4

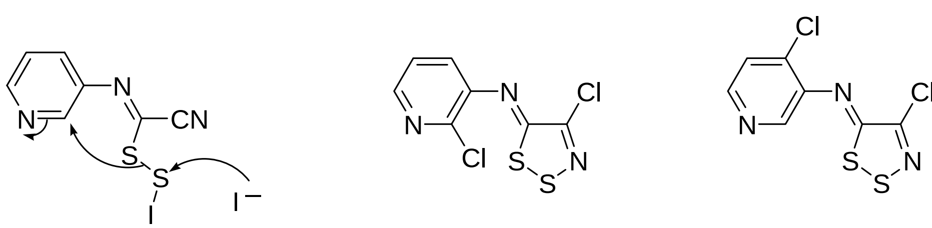
Where the aryl group is electron deficient the major product is the imidoyl chloride carbonitrile **14**.[11] The mechanism that has been proposed by Rees is shown in Scheme 4. To our knowledge no examples of the thermolysis of *N*-heteroaryl-1,2,3-dithiazol-5*H*-imines have appeared in the academic or patent literature.

Thermolysis of *N*-(pyrid-3-yl)-4-chloro-1,2,3-dithiazol-5*H*-imine **15** gave thiazolo-[5,4-*b*]pyridine-2-carbonitrile **16** and thiazolo[4,5-*c*]pyridine-2-carbonitrile **17** in low yields as might be expected based on the mechanism to give benzothiazole **13**. Repeating the reaction in the presence of a soft nucleophile benzyltriethylammonium iodide at 132 ^{o}C in chlorobenzene gave improved but still moderate yields of both isomers. Under these conditions the dithiazole ring is anticipated to suffer an assisted nucleophilic ring opening-ring closure (ANRORC)[12] like mechanism involving the intermediate disulfide **18**. The nucleophilic sulfur that is generated (S-1) is trapped at the electrophilic pyridyl C-2 and C-4 positions and a subsequent oxidation restores the aromaticity of the thiazolopyridine systems.



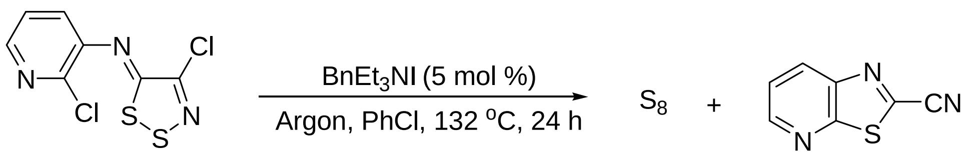
15 **16** (5-11 %) **17** (9-15 %)

15 $\xrightarrow[\text{PhCl, 132 }^{o}\text{C, 40 min}]{\text{BnEt}_3\text{NI (1 equiv.)}}$ S_8 + **16** (25 %) + **17** (29 %)

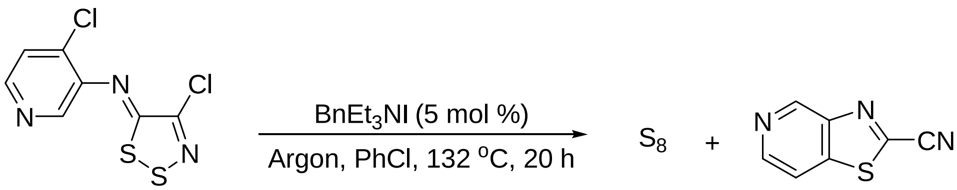


18 **19** **20**

Introducing a chlorine substituent at either C-2 or at C-4 on the pyridyl ring was expected to assist in directing the ring closure and furthermore adjusts the oxidation level of the starting systems thus avoiding the need for oxidative rearomatisation. The 2-chloro and 4-chloro-derivatives **19** and **20** were readily prepared starting from the corresponding aminochloropyridines and dithiazolium chloride **3**. Gratifyingly treatment with catalytic iodide (5 mol %) gave the expected single isomers in near quantitative yields.

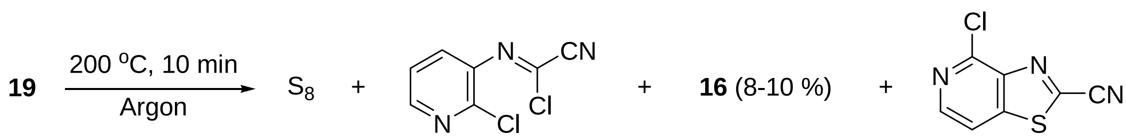


19 **16** (98 %)



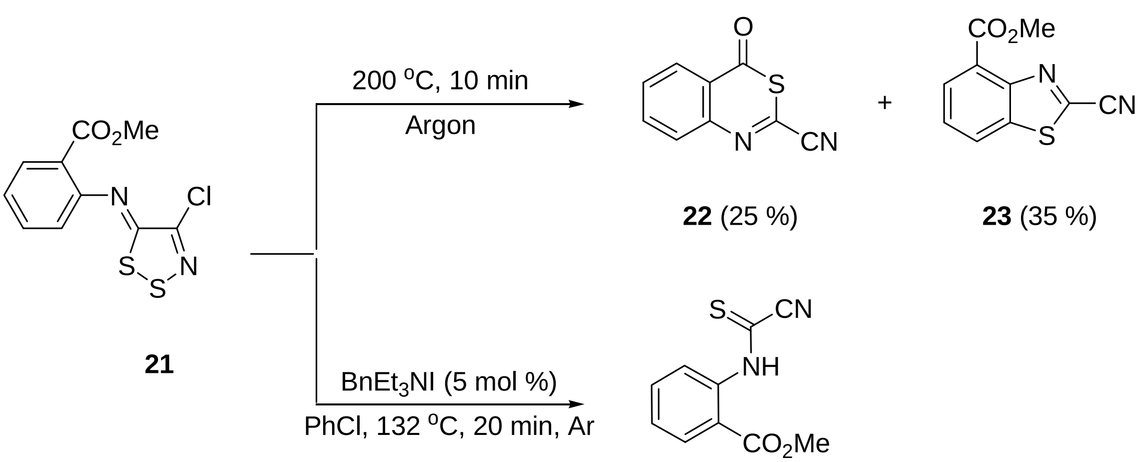
20 **17** (99 %)

Thermolysis of either the 2-chloro and 4-chloro- derivatives **19** and **20** did not yield regiospecific ring closures but mixtures of products were isolated adding further support to the ANRORC type mechanism proposed above.



74-77 % 13-15 %

We attempted to extrapolate the above success to the preparation of 3,1-benzothiazin-4-ones starting from the readily available methyl ester **21** where the electrophilic trap was now the carboxylate group. Initial thermolysis of the ester **21** gave some of the desired benzothiazinone **22** together with the benzothiazolecarbonitrile **23**.

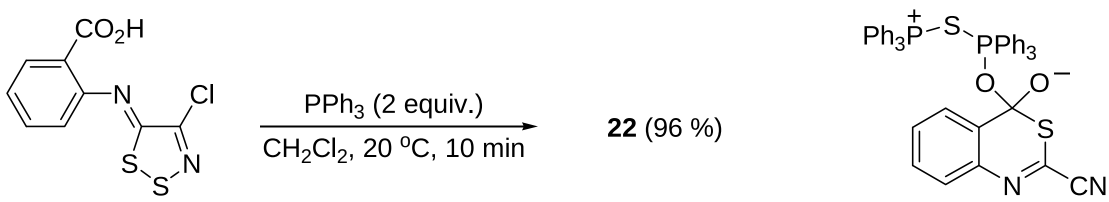


22 (25 %) **23** (35 %)

21

24 (99 %)

On treatment with various soft nucleophilies the major product was however the *N*-arylcyanothioformamide **24**. This could be obtained in near quantitative yield with the use of catalytic benzyltriethylammonium iodide (5 mol %) providing a good route to this useful intermediate.



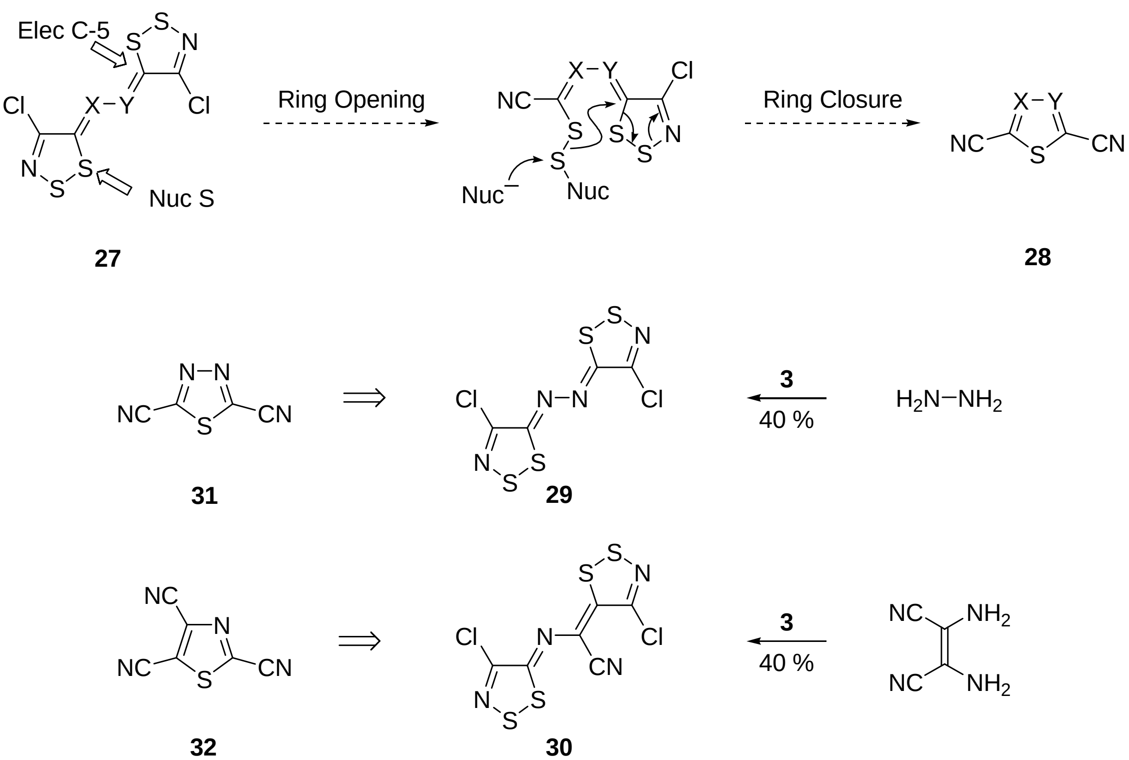
25 **26**

Interestingly Besson, Rees *et al.* reported a quantitative conversion of the iminocarboxylic acid **25** into benzothiazinone **22** on treatment with triphenylphosphine and proposed that the phosphonium salt byproducts help activate the carboxylic acid towards attack (*cf.* intermediate **26**).[13] In our case the methyl ester **21** on treatment with triphenylphosphine gave only a moderate yield of the cyanothioformamide **24**.

2. Synthesis of percyano thiazole and 1,3,4-thiadiazole

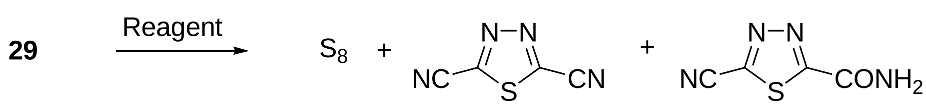
The 1,2,3-dithiazole ring can act as both a source of nucleophilic sulfur at S-1 and as electrophilic trap at the ring carbon C-5.

On treatment with soft nucleophiles bisdithiazole systems such as **27** can therefore be considered as possible precursors to heterocyclic systems of type **28** (Scheme 5). Two bisdithiazoles of this type compound **29**[14] and compound **30**[15] have been reported in the literature and each could provide rapid routes to the corresponding percyano-1,3,4-thiadiazole **31** and percyanothiazole **32** respectively.



Scheme 5

Treatment of either bisdithiazole **29** or **30** with soft nucleophiles such as chloride, bromide or iodide gave the expected percyano-1,3,4-thiadiazole **31** and thiazole **32** systems respectively. These percyano heterocycles suffered hydrolysis during chromatographic isolation to afford a moderate quantity of the corresponding carboxamides **33** and **34** respectively.



31 **33**

Table 1. Transformation of bisdithiazole **29** into 1,3,4-thiadiazoles **31** and **33**

Reagent	Conditions	Yields (%)	
		31	**33**
$BnEt_3NI$ (1 eqiuv.)	Ar, PhCl, 132 °C, 40 min	79	19
$BnEt_3NI$ (0.25 eqiuv.)	Ar, PhCl, 132 °C, 6 h	76	18
Ph_3P (5 eqiuv.)	CH_2Cl_2, 20 °C, 5 min	Trace	0
Ph_3P – polymer bound (6 mol equiv.)	CH_2Cl_2, 20 °C, 10 min	69	0

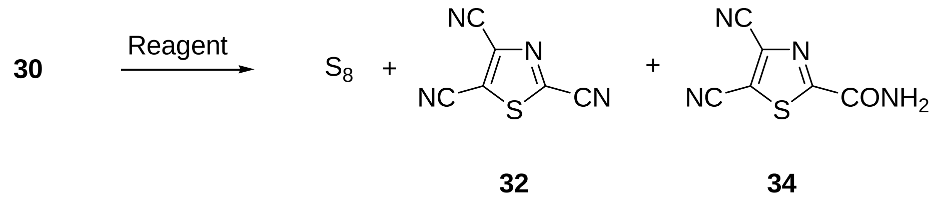


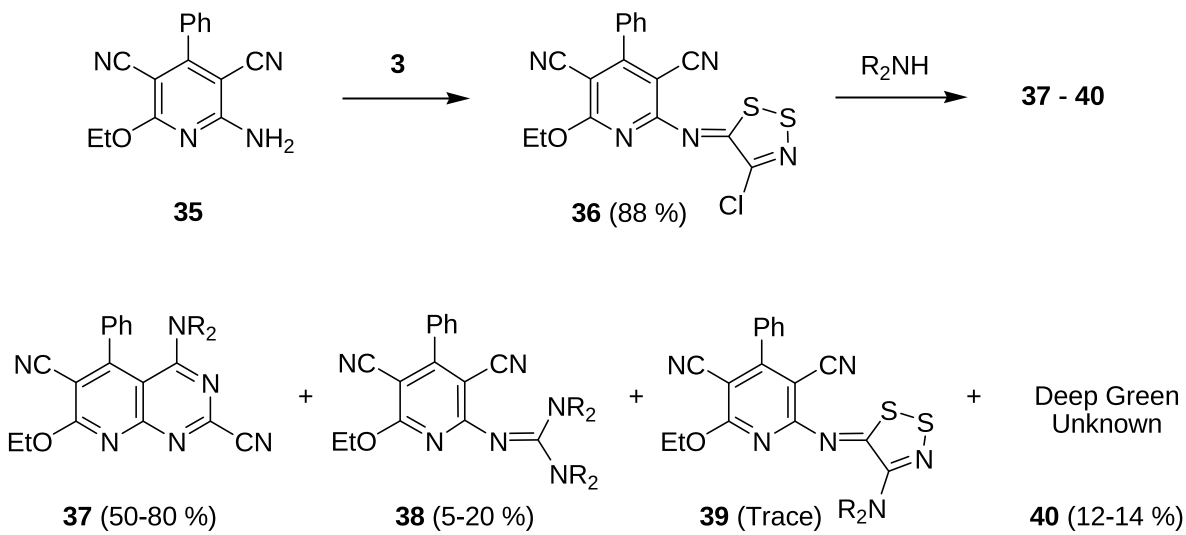
Table 2. Transformation of bisdithiazole **30** into thiadiazoles **32** and **34**

Reagent	Conditions	Yields (%)	
		32	**34**
$BnEt_3NI$ (1 eqiuv.)	Ar, PhCl, 132 °C, 15 min	70	15
$BnEt_3NBr$ (0.5 eqiuv.)	Ar, PhCl, 132 °C, 15 min	68	20
Ph_3P (5 eqiuv.)	CH_2Cl_2, 20 °C, 10 min	Trace	0
Ph_3P – polymer bound (5 mol equiv.)	CH_2Cl_2, 20 °C, 4h	76	0

Chromatography could be avoided by using polymer bound triphenylphosphine as the soft nucleophile since the polymer resin could be separated by filtration to afford a *clean* solution of the desired percyano heterocycle. Recrystallisation of this gave pure product free of any impurities or carboxamide. Surprisingly free triphenylphosphine gave only traces of product.

3. Synthesis of fully substituted pyrido[2,3-*d*]pyrimidines 37: unexpected byproducts

The dithiazolimine **36** prepared from the available fully substituted 2-aminopyridine **35** gave on treatment with cyclic secondary amines the expected fully substituted pyrido[2,3-*d*]pyrimidines **37** in moderate to good yields together with minor quantities of the guanidine **38** and the 4-aminosubstituted dithiazolimine **39** (Scheme 6).



Scheme 6

We have shown that the guanidine **38** is a product of the reaction of pyrido[2,3-*d*]pyrimidine **37** with excess amine presumably by nucleophilic attack by R_2NH at the electrophilic pyrimidine C-2, with pyrimidine ring opening and release of R_2NH from C-4. Surprisingly when acyclic secondary amines such as diethylamine are used in the reaction of dithiazolimine **36** a new previously unobserved green colored byproduct **40** is observed in addition to the byproducts **37**-**39**.

Due to very low solubility NMR or MS spectroscopic data were not obtainable and the structure was solved by single crystal X-ray crystallography to afford the unexpected quinoidal 2,2'-bithiazole **40**.

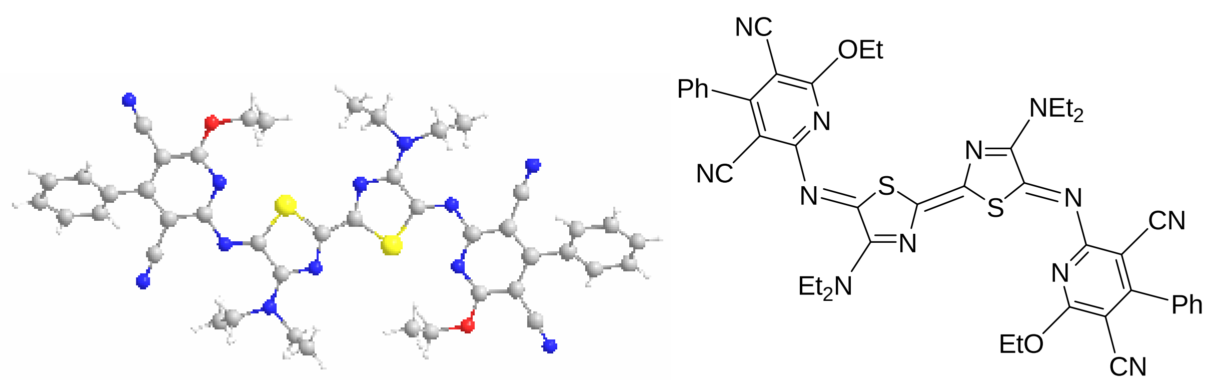
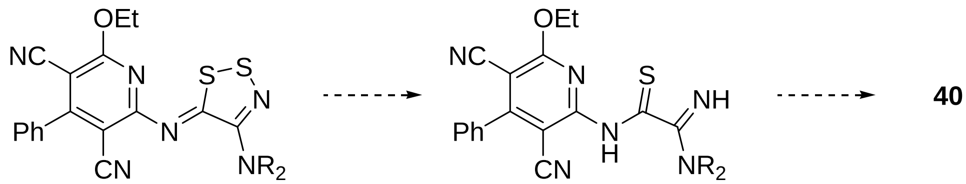


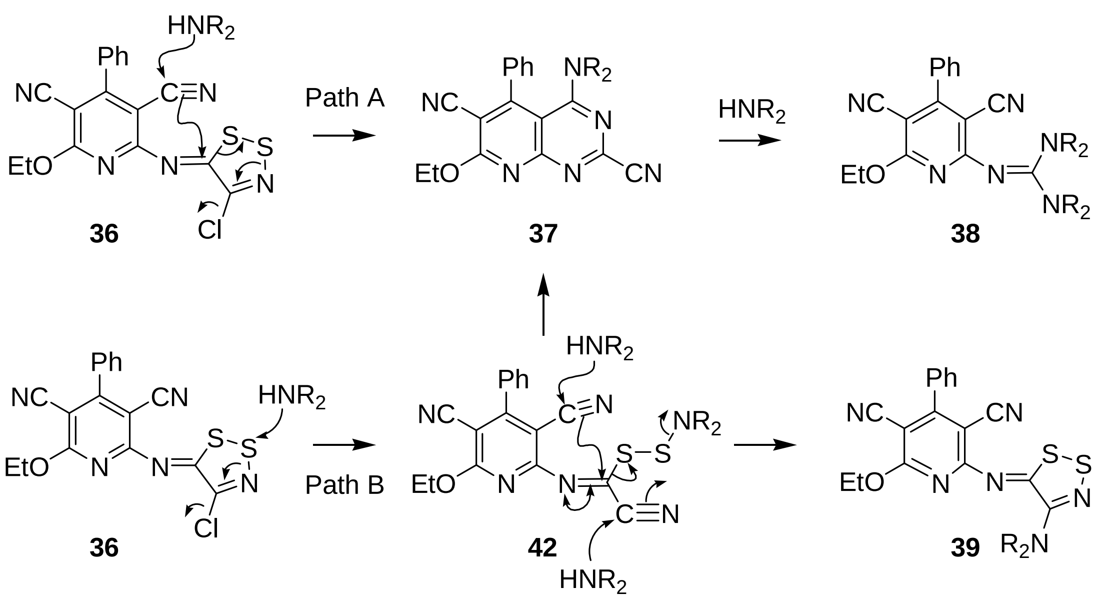
Figure 1. X-Ray structure of 2,2'-bithiazole **40**.

This is the first time such a product type has been observed in 1,2,3-dithiazole chemistry, which raises new questions about the possibilities of the use of 1,2,3-dithiazoles in synthesis. A possible precursor to this compound is the 4-aminosubstituted dithiazolimine **39** which could have been cleaved to afford the ring opened intermediate **41**. These intermediates have been prepared starting from the 4-aminosubstituted dithiazolimines by Kim using alkali bases in alcohol.[16] The two central carbons forming C-2 of the thiazole rings are presumed to be derived from the solvent CH_2Cl_2. However, attempts to improve the yield of the 2,2'-bithiazole **40** by replacing the solvent with different sources of carbon such at $CHCl_3$, CCl_4, CH_2ClBr, CH_2ClI, CH_2Br_2, and $CHBr_3$ gave very similar reaction mixtures but surprisingly no trace of the green product, though formation of the green product **40** in the presence of CH_2Cl_2 was reproducible.



39 **41**

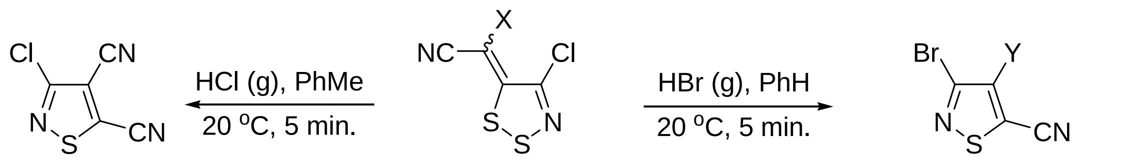
The formation of the pyrido[2,3-*d*]pyrimidine **37** from dithiazolimine **36** is in itself mechanistically interesting as two possible pathways can be envisaged. In the first (Path A) the nitrile group neighbouring the dithiazolimine is initially attacked by the amine and cyclises onto the dithiazole C-5 carbon which instigates opening of the dithiazole ring. A second possibility (Path B) involves attack by the amine at the dithiazole ring sulfur S-2 to afford the disulfide intermediate **42** which then suffers ring closure to afford either the 4-aminodithiazolimine **39** or the pyrido[2,3-*d*]pyrimidine **37** depending on which nitrile is attacked preferably by the incoming amine (Scheme 7). Further studies are needed to determine which is the predominant mechanism.



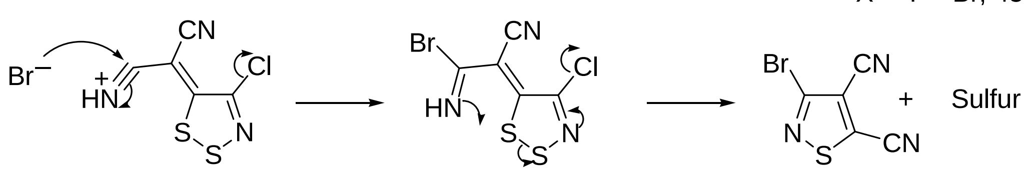
Scheme 7

4. Chemistry of dithiazolylidenacetonitriles 43: Formation of isothiazoles

An example where more extensive studies have provided insight into the ring opening mechanisms of dithiazoles is the chemistry of dithiazolylidenacetonitriles **43**.[17-19] Treatment of dithiazoles **43** with anhydrous HBr afforded the 3-bromoisothiazoles **45** in moderate to good yields. However, with the dithiazolylidenemalononitrile **43** (X = CN) the analogous treatment with anhydrous HCl gives only a trace of the expected isothiazole **44**.[19] Here we argue that the reaction mechanism proceeds by formation of the imidoyl bromide **46** which then cyclises onto the dithiazole ring sulfur S-1. Anhydrous HCl being a weaker acid than HBr is unable to drive this transformation.

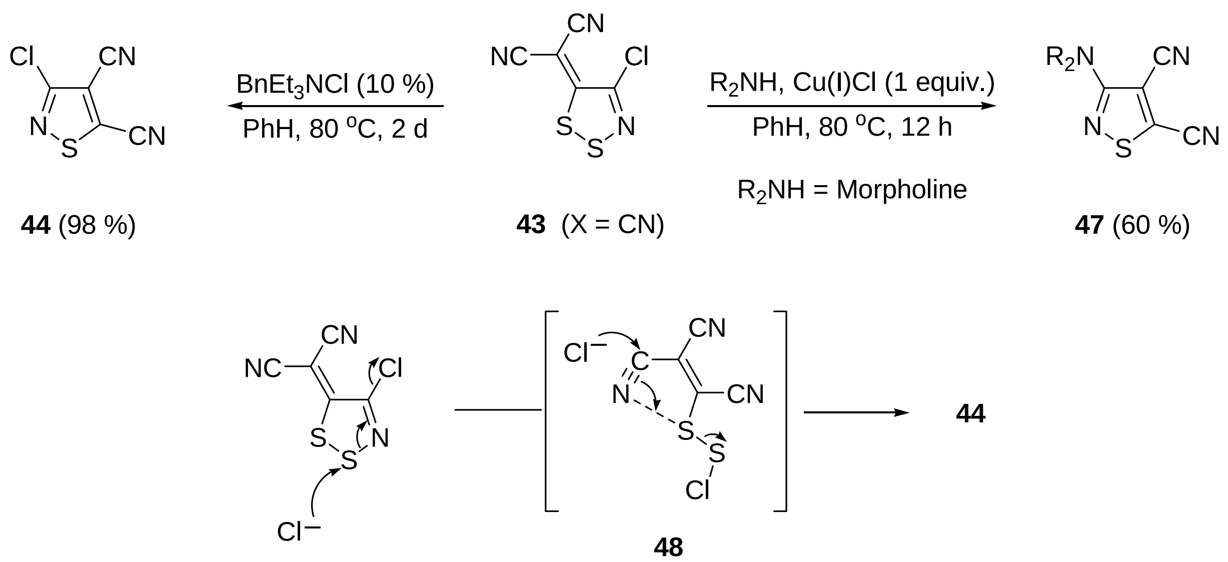


44 **43** X = H, Cl, Br, CN **45** X = Y = CN, 83 %
X = Y = H, 37 %
X = Cl, Y = Br & Cl
X = Y = Br, 45 %



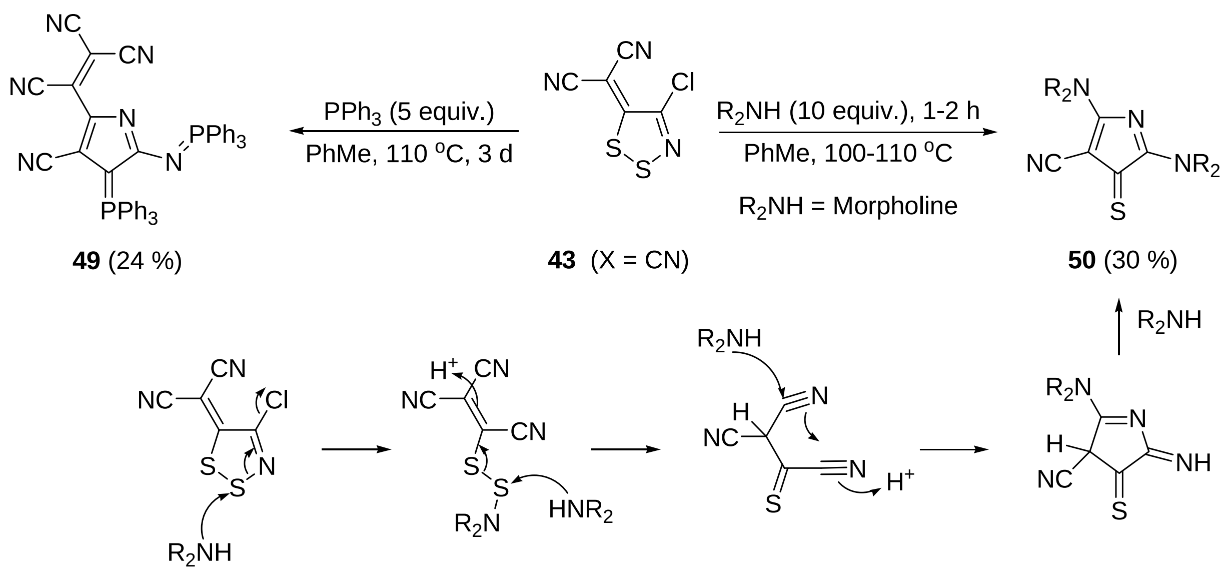
43 (X = CN) **46** **45**

Earlier work on dithiazolylidenemalononitrile **43** (X = CN) showed clearly that catalytic chloride ($BnEt_3NCl$ 10 mol %) was sufficient to convert the dithiazole **43** (X = CN) into 3-chloroisothiazoledicarbonitrile **44** almost quantitatively. Treatment of dithiazolylidenemalononitrile **43** (X = CN) with secondary amines such as morpholine also afforded the 3-morpholinoisothiazoledicarbonitrile **47** although in moderate yield (60%).[17]



Scheme 8

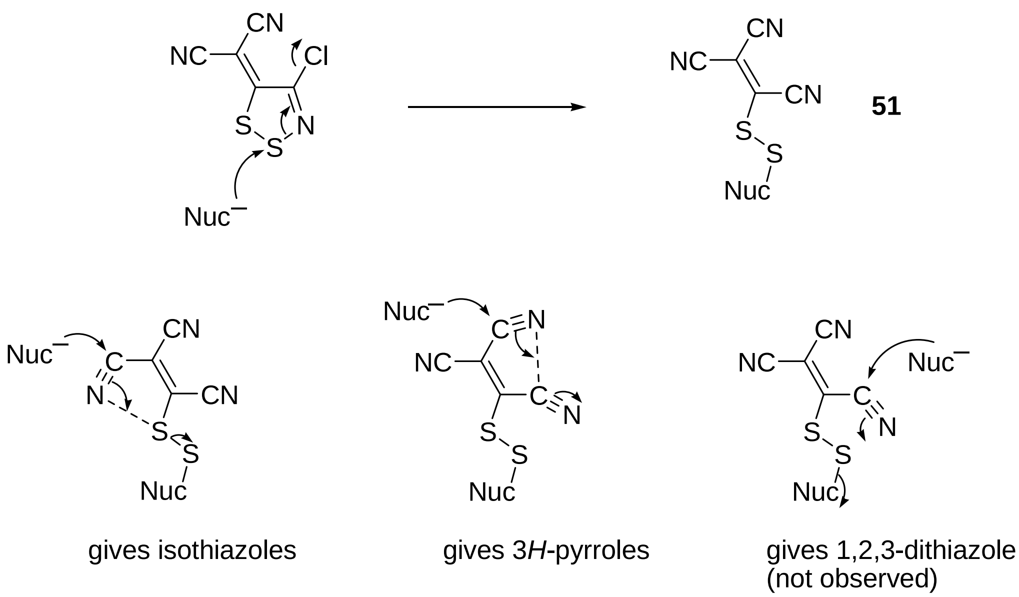
An alternative mechanism was proposed involving the disulfide **48**. Nucleophilic attack on the ring sulfur at S-2 generates the disulfide **48** which can then recyclise to afford the isothiazole **44** (Scheme 8).



Scheme 9

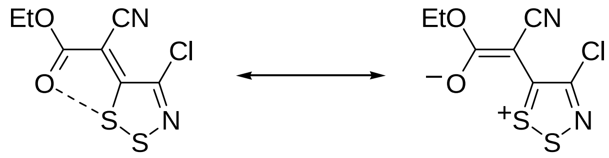
During the investigation of this reaction mechanism two unexpected 3*H*-pyrroles were isolated.[18] The first, a deep blue colored 3*H*-pyrrole **49** whose structure was determined by single crystal X-ray crystallography, was from the reaction of triphenylphosphine with dithiazolylidenemalononitrile **43** (X = CN). The second, on treatment of the dithiazole **43** (X = CN) with excess morpholine, was the orange colored 3*H*-pyrrole **50**.

In light of difficulties in displacing the 4-chloro substituent of neutral 5*H*-1,2,3-dithiazoles a rational mechanism for the formation of these 3*H*-pyrroles **49** and **50** required the involvement of the ring opened disulfide [*cf.* the proposed mechanism of the bismorpholino-3*H*-pyrrole **50** (Scheme 9)]. As such the dithiazolylidenemalononitrile **43** (X = CN) can ring open to afford an intermediate disulfide **51** that could afford isothiazoles, 3*H*-pyrroles and even (although this has not been observed yet) 1,2,3-dithiazole ring systems depending on the cyclisation modes of the tricyanovinyl group (Scheme 10).



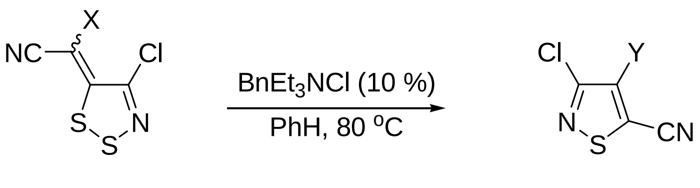
Scheme 10

In order to investigate the reaction further, a series of substituted dithiazolyliden-acetonitriles was prepared and treated with benzyltriethylammonium chloride. Unfortunately for the halo and non-substituted acetonitrile derivatives **43** (X = H, Cl, or Br) the geometry of the attached nitrile group has not been determined (*ie. cis* or *trans* with respect to the dithiazole ring sulfur) but in each case only one isomer was observed by NMR and by chromatography. Owing to a strong non-bonding interaction between the ester carbonyl group with the dithiazole ring sulfur S-1 the ethyl carboxylate **43** (X = CO_2Et) is known to have a *trans* geometry for the nitrile group and the ring sulfur,[20] however, this system was unreactive to halide.



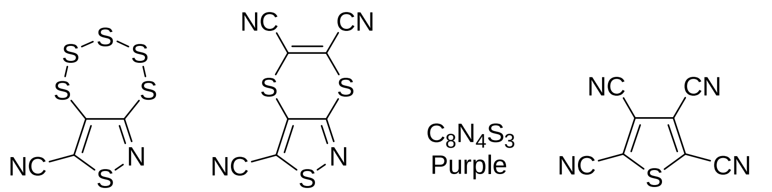
43 (X = CO_2Et)

The acetonitrile derivatives **43** (X = H, Cl, or Br) gave surprisingly complex reaction mixtures. At best 3,4-dichloroisothiazolecarbonitrile **52** (Y = Cl) could be obtained in a respectable yield (63 %), but it was clear that halide exchange was proceeding from the bromoacetonitrile derivative.



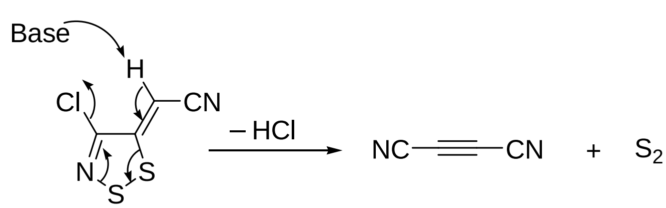
X = CO_2Et, NO REACTION
X = Y = CN, 98 %, (48 h)
X = Y = H, COMPLEX
X = Cl, Y = Cl, 63 % (7 h) COMPLEX
X = Br, Y = Br & Cl, COMPLEX

43 X = H, Cl, Br, CN, CO_2Et **52**



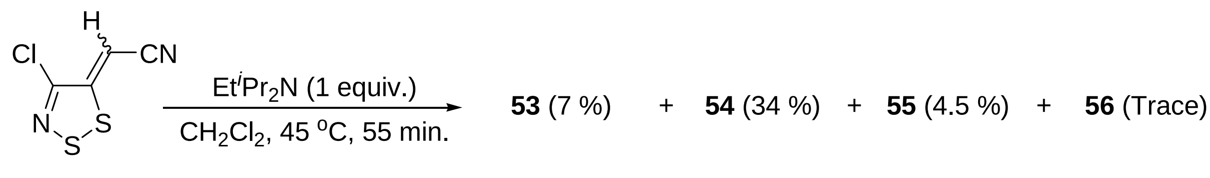
53 **54** **55** **56**

Analysis of the complex mixtures from the reaction of dithiazoles **43** (X = H, Cl or Br) and tetraalkylammonium chloride revealed the presence of several unexpected compounds, the isothiazolopentathiepin-8-carbonitrile **53**, the isothiazolodithiin-4,5,7-tricarbonitrile **54**, an unidentified purple compound **55** and tetracyanothiophene **56**. The isothiazolopentathiepin **53** is known to react with dicyanoacetylene to give dithiin **54** and traces of tetracyanothiophene **56**.[21] These unusual products **53** – **56** are formally composed of one or two units of dicyanoacetylene and sulfur. As such the possibility that dithiazolylidenacetonitrile **43** (X = H) could be *unzipped* by deprotonation to afford dicyanoacetylene, diatomic sulfur and HCl was investigated.



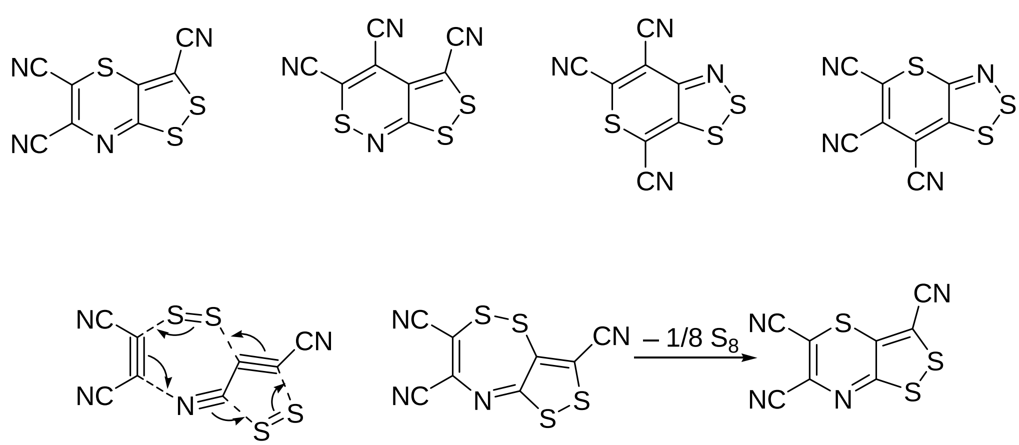
43 (X = H)

Treatment of the dithiazolylidenacetonitrile **43** (X = H) with sterically hindered ethyldiisopropylamine (Hünigs base) gave the compounds **53** – **56** but no trace of the monocyclic isothiazole **52**.



43 (X = H)

The unknown purple colored compound **55** is unstable on silica and hydrolyses during chromatographic isolation to afford a stable purple colored carboxamide **57**. Neither compounds **55** and **57** have been identified but each show eight separate carbon resonances in the C-13 NMR and both show the presence of nitriles in the IR spectra. The molecular formulae have been deduced from mass spectrometry (**55** $C_8N_4S_3$ and **57** $C_8H_2N_4OS_3$). Compound **55** formally contains two units of dicyanoacetylene and three sulfur atoms. The highly colored nature of the compound **55** leads to at least four possible structures (Scheme 11) that presumably could arise from a 4 component 10*π* cycloaddition between two equivalents of diatomic sulfur and two equivalents of dicyanoacetylene to give a fused seven-five heterocycle that then suffers ring contraction through loss of one sulfur atom to give the proposed six-five system. The identity of the purple compounds is being investigated.



Scheme 11

This chemistry looks promising as a possible new route to both pentathiepins and to new methods for the *in situ* generation of acetylene derivatives. Understanding the mechanisms leading to the formation of these unexpected products will aid in the design of 1,2,3-dithiazoles which can be used to build new heterocyclic compounds.

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