Poly-Sulfur-Nitrogen Heterocycles *via* Sulfur Chlorides and Nitrogen Reagents

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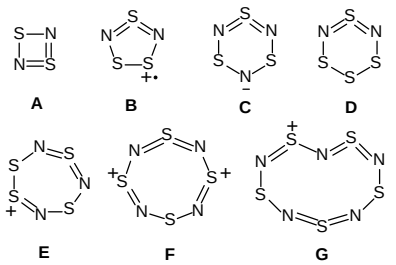
Abstract: The family of poly-sulfur–nitrogen heterocycles includes highly stable aromatic compounds that display physicochemical properties with relevance in the design of new materials, especially those relating to molecular conductors and magnets. The interesting characteristics found in many of these heterocycles have led to the development of modern synthetic methods that are the subject of this review. Heterocycles such as 1,2,3- and 1,2,5-thiadiazoles, 1,2,3- and 1,3,2-dithiazoles, 1,2,3,5-dithiadiazoles, thiatriazines, trithiadiazines, dithia(and trithia)diazepines, trithiatriazepines, dithia(and trithia)tetrazozines, and fused systems are most commonly synthesized from tetrasulfur tetranitride and organic substrates (alkynes, diazomethanes), and from sulfenyl chlorides, sulfur or disulfur dichlorides and nitrogen containing reagents such as bis(trimethylsilyl)sulfurdiimide, trimethylsilyl azide, trisilylated amidines, *N*-imidoylamidines, hydrazones, oximes, and amines.

Contents

Nitrogen and sulfur organic aromatic heterocycles are formally derived from aromatic carbon cycles by a heteroatom taking the place of a ring carbon atom or a complete CH=CH group. The presence of heteroatoms results in significant changes in the cyclic molecular structure due to the availability of unshared pairs of electrons and the difference in electronegativity between heteroatoms and carbon. Therefore, nitrogen and sulfur heterocyclic compounds display physicochemical characteristics and reactivity far from the parent aromatic hydrocarbons. On the other hand, the presence of many nitrogen and sulfur atoms in a ring is normally associated with instability and difficulties in the synthesis but, in fact, surprisingly stable heterocycles with unusual properties can be frequently obtained from simple organic substrates and the appropriate inorganic reagent. This paper reviews the most common synthetic methods to obtain poly-sulfur–nitrogen heterocyclic systems that lie in the middle way between organic and inorganic chemistry. Carbon atoms confer high stability to such rings, according to the aromaticity and antiaromaticity rules, and the nitrogen-sulfur core gives unusual properties to the compounds, in accordance with their electron rich π-excessive nature. The physicochemical properties of this family of compounds have relevance in the design of new materials, specially concerning organic conductors. In contrast with the number and variety of such heterocycles, the number of synthetic methods to afford them is, in practice, restricted to the availability of the appropriate sulfur reagent. The classification of synthetic methods follows the applications of the most common sulfur reagents to the synthesis of heteroaromatic carbon–nitrogen–sulfur rings and sometimes extends to selenium or phosphorus related heterocycles. Binary inorganic sulfur–nitrogen cycles are covered by some reports from Chivers and Oakley [1]. Some binary S–N rings, as **B**–**F** in figure 1, constitute the models and sometimes precursors of the organic members of the series.



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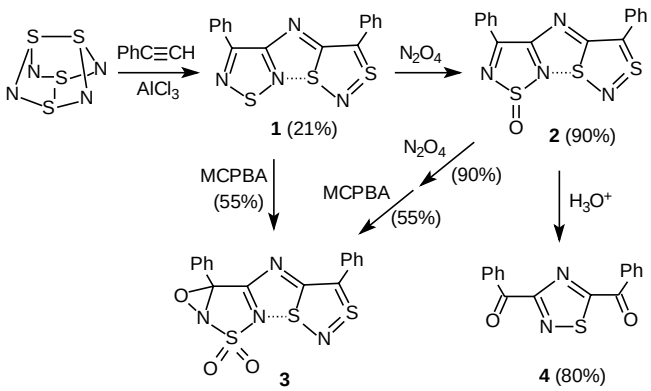
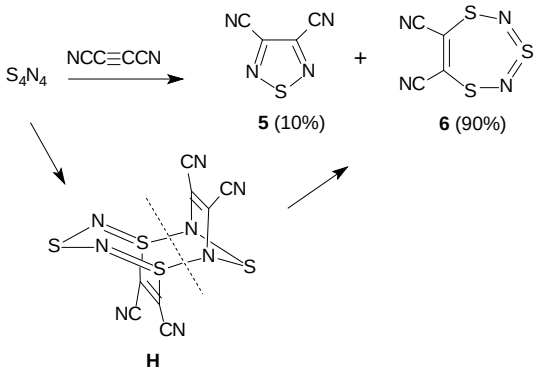
1. Heterocycles from Tetrasulfur Tetranitride and Organic Substrates

Tetrasulfur tetranitride, S_4N_4, is the best known of a whole family of sulfur nitrides and is one of the most studied of all inorganic heterocyclic compounds [2], being readily prepared from sulfur dichloride and ammonia as orange crystals. It may explode when heated, struck, or ground and must be handled with suitable precautions. The atoms of S_4N_4 form a cage structure, with the four nitrogens in a square plane bisecting a tetrahedron of sulfurs, two above and two below the plane. The 12 π electrons are completely delocalized, all the S–N bonds being of equal length. The reactions of tetrasulfur tetranitride with organic substrates have constituted a very valuable source of organic compounds rich in sulfur and nitrogen. The reaction of S_4N_4 with organic substrates, such as acetylenes, ketones or ketoximes, and phenols has been a useful way for the preparation of 1,2,5-thiadiazoles [3]. As expected, the reaction of phenylacetylene and S_4N_4 in refluxing toluene gave 3-phenyl-1,2,5-thiadiazole (16%) as the main product, but in the presence of $AlCl_3$ the same reagents afforded the highly rearranged, thermally stable imine **1** in which both heterocyclic rings and the bridging nitrogen atom are accurately coplanar in the crystalline state [4]. The imine **1** appears to be stabilized by electron delocalisation from the dithiazole to the thiadiazole ring, and this results in molecular planarity and a close interannular *S···N* approach. Imine **1** is converted by nitrogen tetroxide, N_2O_4, into the monoxide **2** and with excess of N_2O_4 into the corresponding *S*-dioxide that was readily oxidized with *m*-chloroperbenzoic acid (MCPBA) to a trioxide with the unusual hetero-fused oxaziridine structure **3**. Trioxide **3** was also prepared directly from imine **1** with an excess of MCPBA. Such trioxidation is presumably a manifestation of the enhanced nucleophilicity of the thiadiazole ring resulting from a highly dipolar structure. The most striking consequence of coulombic attraction between the heterocyclic rings is seen in the ready acidic hydrolysis of monoxide **2** to the 1,2,4-thiadiazole derivative **4**, which is formed from the incipient central ring of the monoxide [5].



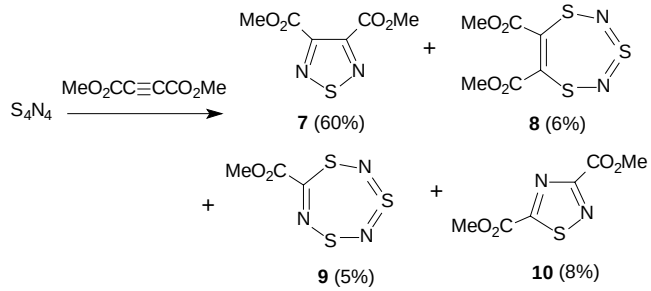
Scheme 1

A completely different reaction took place between S_4N_4 and alkynes bearing electron-withdrawing substituents. Thus, S_4N_4 reacted with highly reactive alkynes, such as dicyanoacetylene, to give the expected 1,2,5-thiadiazole **5**, in addition to high yields of the novel 6,7-dicyano-1,3,5,2,4-trithiadiazepine structure **6**. The reaction can be rationalized by 1,5-cycloaddition of one alkyne to S_4N_4 across sulfur, to give **6**. Alternatively, a 2,4-cycloaddition of another alkyne across nitrogen could give **5**. An intermediate like **H**, which could dissociate directly into the aromatic products observed, accounts for both types of mechanisms [6].



Scheme 2

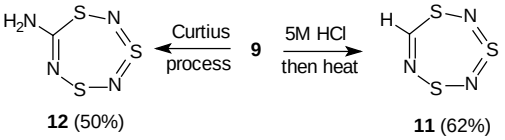
Dimethyl acetylenedicarboxylate (DMAD) gave a mixture of four products, **7**–**10**, in its reaction with S_4N_4, 1,2,5-thiadiazole **7** being the main product [2, 7]. Acetylenes activated with other electron releasing groups, as acetyl or formyl groups, behave in an analogous manner, affording mixtures of similar products.



Scheme 3

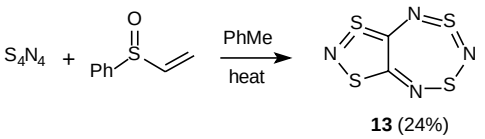
The yield of trithiadiazepine **8** was improved up to 40% by the presence of Lewis acids, particularly titanium(IV) chloride, the formation of trithiatriazepine **9** being totally suppressed [8]. The parent unsubstituted 1,3,5,2,4-trithiadiazepine has been successfully synthesized by rational synthesis (see next section), but an

independent synthesis of the 1,3,5,2,4,6-trithiatriazepine system has not yet been published. Thus, formation of the methyl trithiatriazepine-7-carboxylate (**9**) is the only way to this system. The yield of ester **9** from S_4N_4 and DMAD has been optimized to almost 30% by heating for 24 h in a 2:1 benzene-toluene mixture [9]. Furthermore the ester **9** could be hydrolyzed to the carboxylic acid and the acid decarboxylated to the parent trithiatriazepine **11** by heating in dioxan, all in good yield [9]. Trithiatriazepine is a colorless, thermally very stable crystalline solid. It is assumed to be a 10π aromatic system, similar to trithiadiazepine. It can be nitrated and brominated, and the amine **12** was available from the ester **9** by a classical Curtius process [10]. The chemistry of this heterocycle has been reviewed [11].



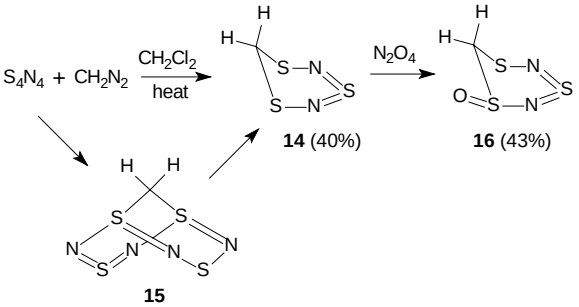
Scheme 4

The reaction of tetrasulfur tetranitride and alkenes which are acetylene equivalents, such as phenyl vinyl sulphoxide or sulphone, has been studied as an alternative way to incorporate a C_2 unit into the S_4N_4 structure. Thus, tetrasulfur tetranitride and phenyl vinyl sulphoxide reacted to give the planar delocalized 14π electron aromatic system, 1,3,5,7-tetrathia-2,4,6,8-tetraazaazulene **13** in which all the S_4N_4 atoms have been retained [12]. Reaction of phenyl vinyl sulphone and S_4N_4 indeed gave the same compound **13**, but in very low yield (4%). The tetrathiatetraaza-azulene **13**, like trithiatriazepine and benzotrithiadiazepine, did not form charge transfer complexes with electron acceptors [12b].



Scheme 5

The reaction of S_4N_4 with diazomethane has been studied as a way of introducing a methylene group into S_4N_4. The product of this reaction was a six membered ring, 1,3,5,2,4-trithiadiazine **14**, a stable red crystalline solid. The ring has a slightly puckered envelope conformation with a nearly planar S_3N_2 unit [13]. The trithiadiazine could be formed *via* nucleophilic attack by diazomethane at sulfur in S_4N_4 followed by displacement of the diazo nitrogen by transannular sulfur to give the intermediate **15** that could lose N_2S to give compound **14**. Trithiadiazine **14**, which was independently synthesized (see next section), formed the equatorial *S*-oxide **16** with dinitrogen tetraoxide or *m*-chloroperbenzoic acid.



Scheme 6

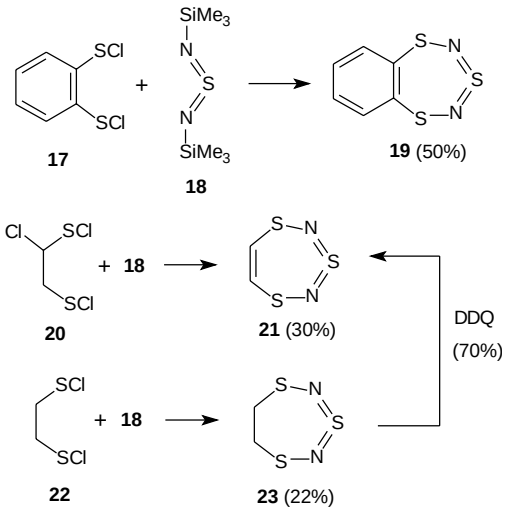
Dimethyl- and phenyldiazomethane and S_4N_4 reacted similarly to give 6,6-dimethyl- or 6-aryltrithiadiazines [13].

Recently the more reactive S–N reagent, trithiazyl trichloride, $S_3N_3Cl_3$, has been similarly applied to heterocyclic synthesis by the Rees group [14].

2. Heterocycles from Sulfenyl Chlorides and Nitrogen Containing Reagents

In contrast to the reactions of tetrasulfur tetranitride and organic substrates, which give unpredictable but highly interesting sulfur–nitrogen heterocycles, in unpredictable yields, the reactions of bis(sulfenyl chlorides) and nitrogen-bearing reagents provide a rational synthesis of many stable heterocycles. The development of stable but reactive reagents of nitrogen, as bis(trimethylsilyl)sulfurdiimide, trimethylsilyl azide and trisilylated amidines, was a great improvement in this chemistry. For example, the trithiadiazine **14** and others are obtained in one step by reaction of substituted methanebis(sulfenyl chlorides) and bis(trimethylsilyl)sulfur diimide in yields sometimes higher than 50% [15]. Trithiadiazepines, obtained in low yields from the reaction of S_4N_4 and electron deficient alkynes (see previous section) are better obtained from sulfenyl chlorides. Thus, benzo-1,3,5,2,4-trithiadiazepine **19** was prepared from benzene-1,2-bis(sulfenyl chloride) **17** and bis(trimethylsilyl)sulfurdiimide **18** under high dilution conditions. The parent trithiadiazepine **21** is obtained in one step from 1-chloroethane-1,2-bis(sulfenyl chloride) **20** and sulfurdiimide **18**, or by dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) of the dihydrotrithiadiazepine **23**, obtained itself from 1,2-ethanedisulfenyl chloride **22** and sulfurdiimide **18** [16]. Trithiadiazepine **21** was a thermally stable, colorless crystalline solid. The molecule is planar, symmetrical (space group $P2_1/n$), and has the intermediate bond lengths

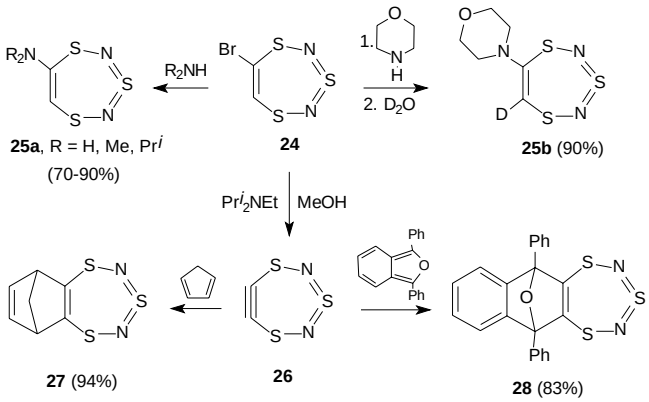
expected for an aromatic structure. The aromatic nature of trithiadiazepines **19** and **21** was confirmed by X-ray diffraction [17] as well as by their chemical and physical properties. Some progress reports [2, 11, 18] and a review on the chemistry of trithiadiazepines have been released [19].



Scheme 7

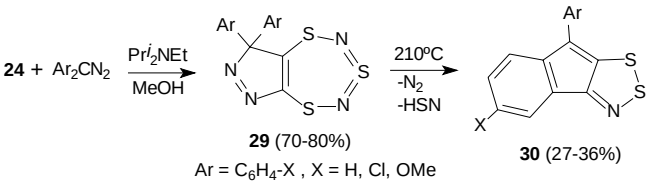
The parent compound **21** readily underwent electrophilic aromatic substitution to give mono- and dinitro and bromo derivatives, and this provided ready access to trithiadiazepines bearing electron-withdrawing groups [20]. It was acylated with acid anhydrides in the presence of trifluoromethanesulphonic acid, and mercuriated to give the 6,7-bis(acetoximercury)trithiadiazepine. In contrast with mercuriation, thalliation of trithiadiazepine afforded only the mono metallated derivative [21]. Though the reduction of 6-nitrotrithiadiazepine did not afford the 6-aminotrithiadiazepine, this compound and substituted amines **25a**,**b** were easily prepared from 6-bromotrithiadiazepine **24** and ammonia or amines. The amines **25a** were produced by an elimination–addition mechanism rather than by nucleophilic substitution. Thus, elimination of HBr gave rise to a hetero-aryne intermediate, to which amines could add nucleophilically. This mechanism was established by deuterium exchange experiments using morpholine as the base, from which the deuteriated 7-morpholinotrithiadiazepine **25b** was prepared [22]. The hetero-aryne 6,7-didehydrotrithiadiazepine **26** was prepared in high yield by using the hindered non-nucleophilic amine *N*-ethyldiisopropylamine (Hünig's base) in methanol and trapped with a variety of electron rich dienes, such as cyclopentadiene to give **27** or diphenylisobenzofuran to give **28** [22].

Heteroaryne **26** could also be intercepted by diaryldiazomethanes, and the resulting pyrazolines, formed



Scheme 8

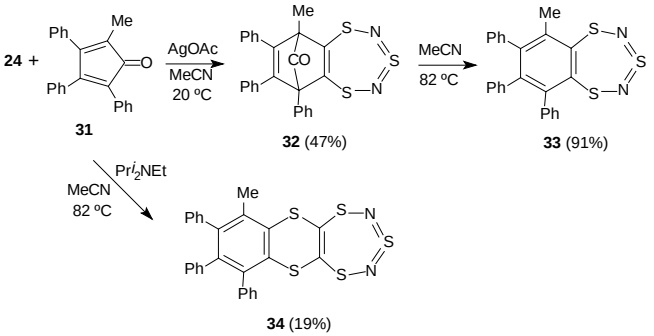
by 1,3-dipolar cycloaddition on the triple bond, underwent a deep-seated molecular rearrangement when heated [23]. Thus, when 6-bromotrithiadiazepine **24** and diaryldiazomethanes were treated with *N*-ethyldiisopropylamine in methanol, the expected cycloadducts **29** were formed as stable colorless crystalline compounds. Since they are cyclic azo compounds they could, on pyrolysis, lose nitrogen to form other derivatives. Compounds **29** readily decomposed at 210 °C losing nitrogen, and an HNS fragment undergoing cyclization onto one of the phenyl rings and forming the highly thermally stable, deeply red colored 8-arylindeno-1,2,3-dithiazoles **30** [23].



Scheme 9

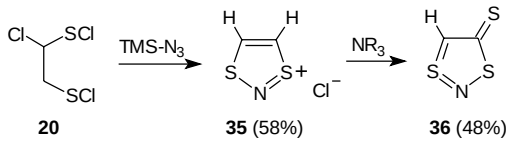
Cyclopentadienones were able to trap the heteroaryne **26**, but the structure of the final product depended strongly on the reaction temperature and stability of initial cycloadduct. For example, reaction of bromotrithiadiazepine **24** with 2-methyl-3,4,5-triphenylcyclopentadienone **31** in cold acetonitrile gave the carbonyl-bridged adduct **32**, that easily lost carbon monoxide to give the decarbonylated product **33**. But in hot acetonitrile two molecules of the aryne were involved resulting in the formation of dithiin **34**. Other cyclopentadienones reacted similarly to give the 1:1 or the 2:1 cycloadduct [24].

The reaction of 1,2-bis(sulfenyl chlorides) with trimethylsilyl azide constitutes one important way to 1,3,2-dithiazol-1-ium salts [25]. By this method, the parent 1,3,2-dithiazol-1-ium chloride **35** was obtained by reaction of 1-chloroethane-1,2-bis(sulfenyl chloride) **20**



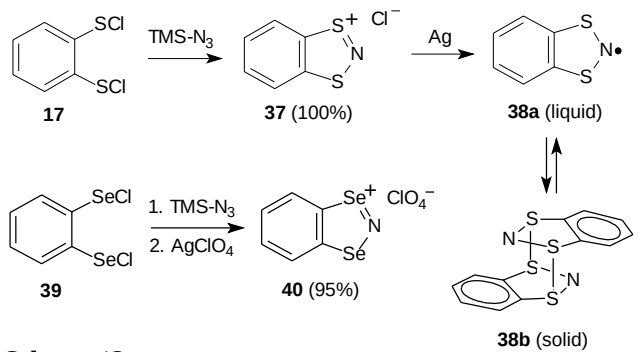
Scheme 10

and trimethylsilyl azide [26]. Treatment of the salt **35** with bases gave the 1,3,2-dithiazole-4-thione **36** [26].



Scheme 11

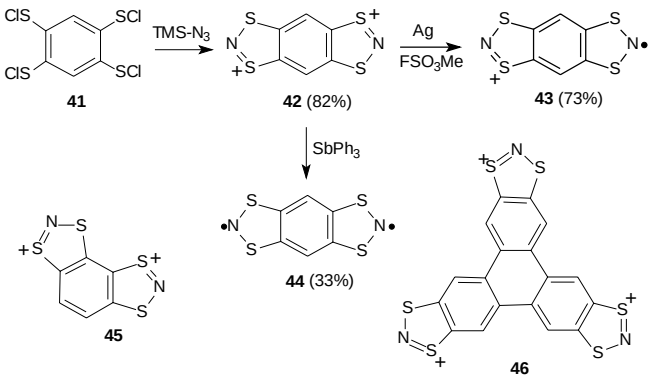
The 1,3,2-benzodithiazol-1-ium chloride **37** was obtained as a stable solid in quantitative yield by reaction of benzene-1,2-bis(sulfenyl chloride) **17** with trimethylsilyl azide [27]. The salt **37** was reduced with silver powder to give the air sensitive radical **38a** that formed highly conducting charge transfer complexes with tetracyanoquinodimethane (TCNQ) [27]. The X-ray crystal structure showed that it was a centrosymmetric 1,3,2-benzodithiazolyl dimer **38b** containing two units joined by two long S–S bonds [28]. Variable temperature magnetic susceptibility measurements showed the solid to be essentially diamagnetic, but on melting the compound became paramagnetic. This and other SNS-containing radical systems are thus referred as paramagnetic liquids [28]. Benzo-1,3,2-diselenazolium chloride **40** was prepared from **39** analogously to the



Scheme 12

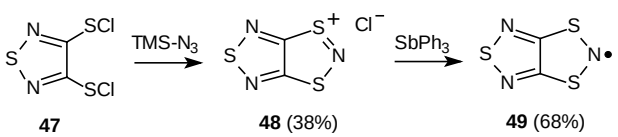
corresponding sulfur compound [29]. The cation **40** has been characterized as its perchlorate by X-ray structure analysis. Reduction of **40** afforded an unstable neutral radical. When the *N*-atom in **40** was replaced by Se^+, a stable benzo-1,2,3-triselenolium radical cation was obtained and its X-ray crystal structure was reported [30].

The reaction of bis(sulfenyl chlorides) and trimethylsilyl azide has been successfully employed for the synthesis of many other 1,3,2-dithiazolium salts and stable radicals, as for example **42**–**46** [31]. The benzo-1,2:4,5-bis(1,3,2-dithiazole) system **42**–**44**, obtained from 1,2,4,5-tetra(sulfenyl chloride) (**41**) and trimethylsilyl azide, has been studied in diverse oxidation states as the dication **42** and the radical cation **43** which is a dimer in the solid state [31]. On the contrary, the heterocyclic diradical **44** consisted of discrete, unassociated molecules in the crystal state [32].



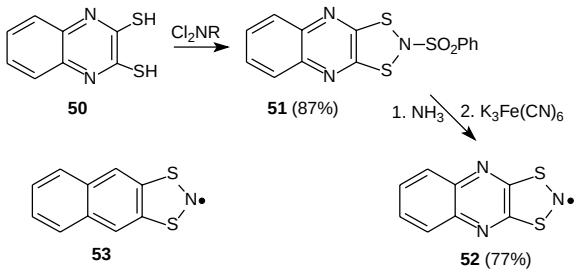
Scheme 13

If suitable bis(sulfenyl chlorides) are accessible, fused heterocyclic 1,3,2-dithiazole derivatives are also obtained. By reaction of the 1,2,5-thiadiazole-3,4-bis(sulfenyl chloride) **47** and trimethylsilyl azide, the 1,3,5-trithia-2,4,6-triazapentalene cation **48** is obtained as an orange solid. Treatment of **48** with sodium dithionite or triphenylantimony led to the air stable deep blue radical **49** that crystallized in the form of black needles. Its X-ray structure showed no association between single radicals, in contrast with the short intermolecular contacts found in other dithiazole radicals [33]. The ESR spectrum of **49** was also consistent with the structure [34].



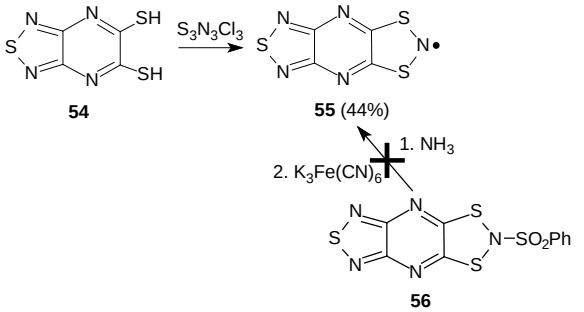
Scheme 14

The reaction of bis(sulfenyl chlorides) and amine derivatives gives *N*-substituted 1,3,2-dithiazole derivatives that, in some instances, have been used as precursors for stable radicals [35]. Starting from 1,2-dithiol **50**, *N*-arylsulfonyl-1,3,2-dithiazole **51** was formed by reaction with *N*,*N*-dichloroarylsulfonamide. Reaction of **51** with ammonia, followed by treatment with potassium ferricyanide, gave the quinoxaline-1,3,2-dithiazolyl radical **52** [35]. Its ESR spectrum was studied [36]. The air stable radical **52** did not dimerise; nor did the air unstable 2,3-naphthalene-1,3,2-dithiazolyl radical **53**, prepared from naphthalene-2,3-bis(sulfenyl chloride) in the usual manner[37].



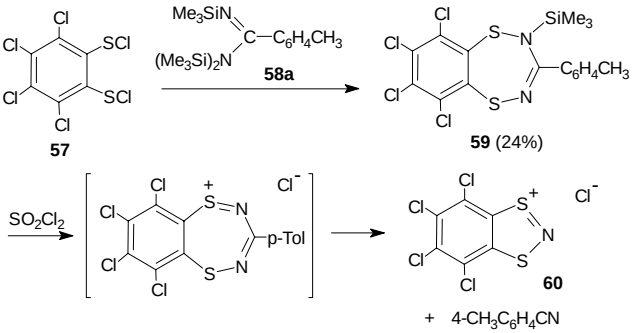
Scheme 15

The stable heterocyclic radical 1,2,5-thiadiazolo-1,3,2-dithiazolopyrazinyl **55** was prepared by treatment of 5,6-dithiolo-1,2,5-thiadiazolo[3,4-*b*]pyrazine (**54**) with trithiazyl trichloride, $S_3N_3Cl_3$, and purified by fractional sublimation in vacuum [38]. This method has not yet been used for other 1,3,2-dithiazoles. Radical **55** was not obtained from the 2-arylsulfonyl-1,3,2-dithiazole **56**. Single-crystal conductivity measurements, as well as variable temperature magnetic susceptibility measurements of radicals **52**, **53** and **55**, have been performed in search for applications as molecular conductors and molecular magnets [37–38].



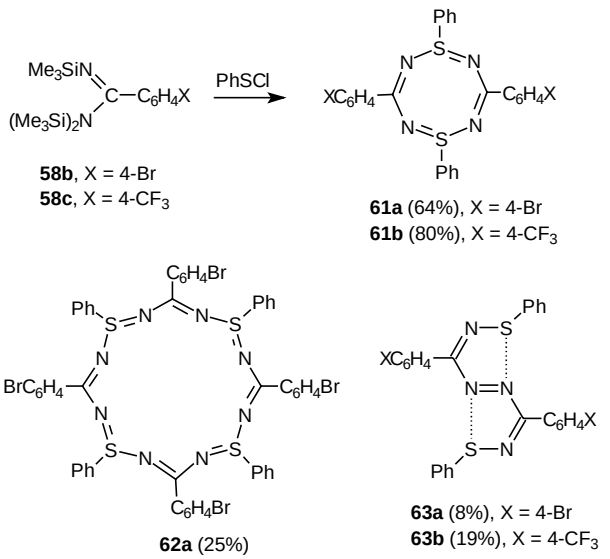
Scheme 16

Tetrachlorobenzene-1,2-bis(sulfenyl chloride) **57** reacted with the trisilylated benzamidine **58a** to give the dithiadiazepine derivative **59** which was characterized by X-ray diffraction [39]. Chlorination of **59** promoted a ring contraction to form *p*-tolunitrile and the unstable tetrachlorobenzo-1,3,2-dithiazolium chloride **60** [39].

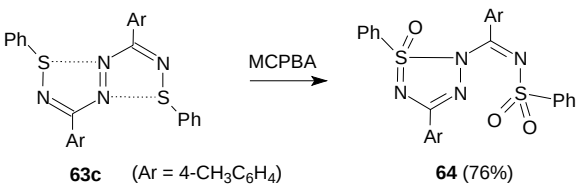


Scheme 17

The reaction of mono-arylsulfenyl chlorides and trisilylated benzamidines has been used for the synthesis of linear compounds, mainly diazenes, but in some cases heterocyclic compounds were obtained in optimum yields. Eight-membered rings **61a**,**b** and the sixteen-membered ring **62a**, in addition of linear diazenes **63a**,**b**, were obtained in variable yields, depending on the reaction conditions, by reaction of phenylsulfenyl chloride and trisilylated benzamidines **58b**,**c** [40].



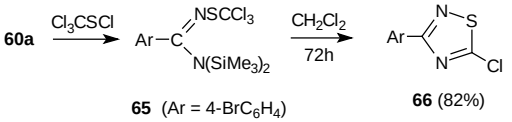
Scheme 18



Scheme 19

On the other hand, the reaction of diazene **63c** with MCPBA resulted in ring closure *via* an intramolecular redox process to give the 1,2,3,5-thiatriazole derivative **64** [41].

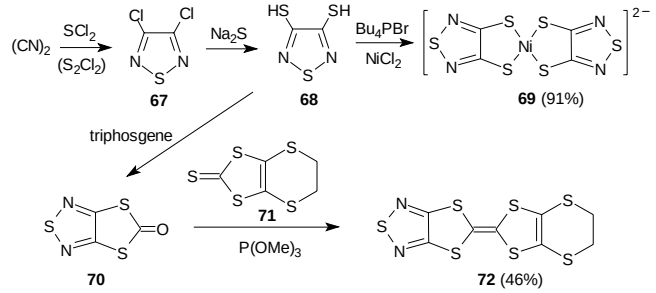
As the last example of this series, Cl_3CSCl reacted with benzamidine **60a** to give the monothiolated benzamidine **65** which on standing in solution underwent intramolecular cyclization to the 1,2,4-thiadiazole **66** [42].



Scheme 20

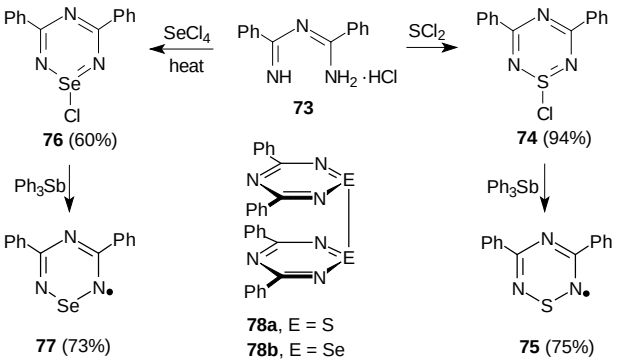
3. Heterocycles from Sulfur Dichloride and Nitrogen Containing Reagents

Sulfur dichloride, SCl_2, is an extremely reactive electrophile towards alkenes, dienes, azadienes and nitriles [43]. Compounds containing the NCCN system in which the N–C groups exist at any hybridization, *sp*, sp^2 and sp^3 in any combination, such as the 1,2-bis(amines, imines, amides, nitriles and oximes), react with sulfur dichloride (and also with disulfur dichloride) to form substituted 1,2,5-thiadiazoles [43b]. For example, the reaction of oxalic dinitrile and sulfur (or disulfur) dichloride afforded **67** [44a]. Substitution of the two chlorine atoms by sulfide anions gave 1,2,5-thiadiazole-3,4-dithiol **68** that has been the subject of intense research in preparing conducting materials from metal complexes **69** [44b–c]. It has also been included in fused tetrathiafulvalene (TTF) derivatives **72** [44d–e] *via* reaction with triphosgene to give **70**, which was coupled with the 1,3-dithiole-2-thione **71**.



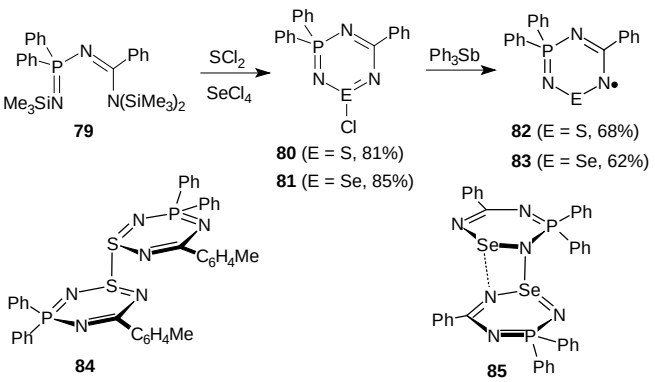
Scheme 21

The reaction of *N*-imidoylamidines **73** and sulfur dichloride has been used for the synthesis of *S*-chloro-1,2,4,6-thiatriazines **74** in remarkably good yield [45, 1e]. The reaction has been extended to the 1-chloro-1,2,4,6-selenatriazines **76** *via* the reaction of *N*-benzimidoylbenzamidine **73** and selenium tetrachloride. Both *S*-chlorothiatriazines **74** and *Se*-chloroselenatriazines **76** were easily reduced by triphenylantimony to the 1,2,4,6-thiatriazinyl **75** and 1,2,4,6-selenatriazinyl **77** radicals, in which the spin density evenly spread over the three nitrogen centers. The radicals **75** and **77** associated in solution and in solid state. The crystal structures were cofacial diamagnetic dimers **78a**,**b** with long S–S or Se–Se interannular bonds [45, 1e].



Scheme 22

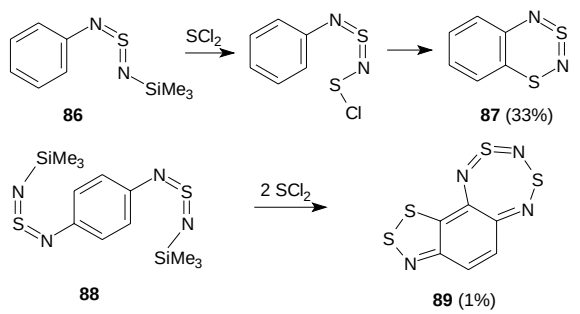
Stable organic radicals possess characteristics that are attractive for the design of synthetic metals. For this purpose, 1,3,2,4,6-thia- and 1,3,2,4,6-selenaphosphatriazinyl radicals have been studied. Thus, the persilylated phosphimidoylamidine **79** reacted with excess of sulfur dichloride to give bright yellow crystals of 1-chloro-3,3,5-triphenyl-1,3,2,4,6-thiaphosphatriazine **80**; similarly, **79** reacted with selenium tetrachloride in refluxing acetonitrile to give yellow crystals of the selenaphosphatriazine **81**, both in high yield [46]. Both **80**, **81** were reduced by triphenylantimony to give strong and persistent ESR signals of the corresponding thia- and selenaphosphatriazinyl radicals **82**, **83**. In the solid state, the sulfur-based compound formed a twisted (for



Scheme 23

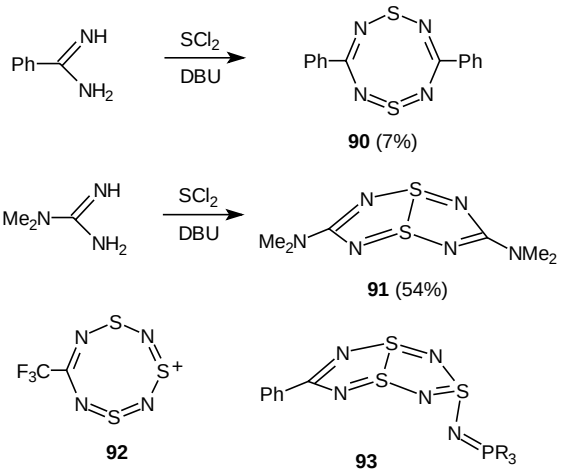
steric reasons) cofacial dimer **84**, with a S–S interannular bond. By contrast, its selenium analogue associated *via* an interannular Se–N bond, to produce the dimer **85**, whose internal structural features resembled those of a 6π-cation/8π-anion pair [46, 1e]. As an extension of the method, 1,4-phenylene-bridged thia- and selenaphosphatriazines and the corresponding bis(thiaphosphatriazinyl) and bis(selenaphosphatriazinyl) diradicals have been obtained [46c].

The coupling of silylated sulfur diimides with sulfur dichloride has been used for the synthesis of heterocycles. The slow addition of *N*-phenyl-*N*'-trimethylsilyl sulfurdiimide **86** [obtained from phenylsulfenyl chloride and bis(trimethylsilyl)sulfurdiimide] to a solution of sulfur dichloride in methylene chloride afforded benzo-1,3-dithia-2,4-diazine **87** as deep blue needles [47]. Dithiadiazine **87**, as well as its 5,6,7,8-tetrafluoro derivative [48a], are 12π-electron, formally antiaromatic, but thermodynamically quite stable compounds. Their chemistry has been investigated only briefly [47–48]. On the other hand, the reaction of the bifunctional *p*-phenylene derivative **88** with sulfur dichloride did not give the corresponding benzobis(dithiadiazine); instead the intense blue, in solution, 1,2,7,9-tetrathia-3,6,8,10-tetraazacyclohept(*e*)indene **89**, having a phenazulene-like structure, was produced as golden needles in very low yield [49].



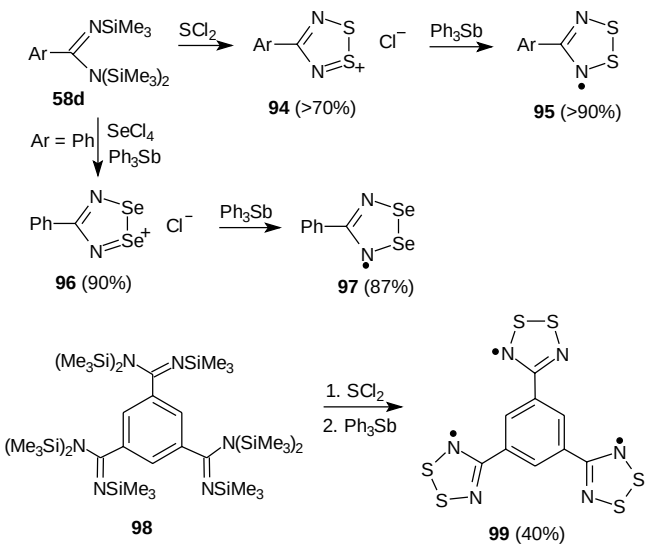
Scheme 24

The condensation of benzamidine with sulfur dichloride at low temperature, in the presence of diazabicycloundecene (DBU), was a complex reaction from which a yellow crystalline solid, 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine **90** was isolated. This 8-membered heterocyclic ring system was perfectly planar, indicating a delocalized (10π) aromatic system [50]. The di-*tert*-butyl compound (14%) [51] or the di-2-thienyl derivative (7%) [52] were synthesized by similar ways and possessed structures analogous to that of the diphenyl compound **90**. Under carefully controlled conditions, using silylated amidines or their *N*-lithium salts, a series of dithiatetrazocine derivatives were obtained in good yield (50–60%) [53]. The reaction of *N*,*N*-dimethylguanidine with sulfur dichloride gave the corresponding 3,7-bis(dimethylamino) compound **91** in fair yield [50], but X-ray diffraction showed that the heterocyclic ring was no longer planar, but folded about an axis through the two sulfur atoms. One dimethylamino substituent was sufficient to buckle the dithiatetrazocine ring [52]. The planar structure has been found in other 8-membered rings, as the trithiatetrazocinium cation **92** [54], and the puckered boatlike ring was also found in related rings, as the 3-substituted trithiatetrazocines **93** [55].



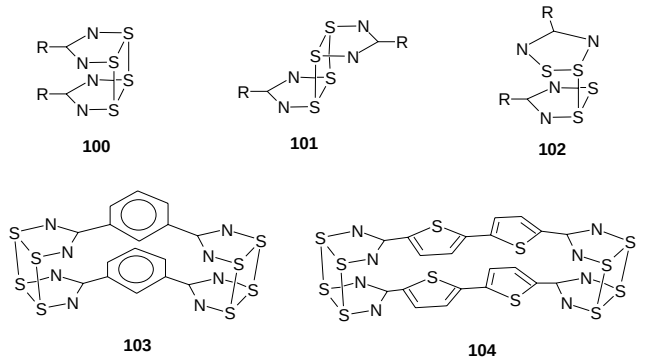
Scheme 25

In a much more general reaction, the condensation of silylated aryl amidines **58d** or their *N*-lithium salts with excess of sulfur dichloride in refluxing acetonitrile afforded 4-aryl-1,2,3,5-dithiadiazolium chlorides **94**. Condensation of silylated amidines **58d** with a mixture of $SeCl_4$ and Ph_3Sb allowed the synthesis of the isostructural diselenadiazolium salts **96**. Reduction of dithiadiazolium (or diselenadiazolium) chloride salts by Ph_3Sb, or other reagents, afforded stable free radicals **95** (and **97**) [56]. The bis- and trisdithiadiazolium salts and their radicals (*e.g.* **99**) could be prepared by reaction of the corresponding persilylated amidine (such as **98**) with excess of SCl_2 and reduction with Ph_3Sb [57]. The sequence constitutes one of the main synthetic routes to the 1,2,3,5-dithiadiazolyl radicals and their selenium analogs. The study of the physical properties of these radicals has been oriented to the design and development of organic metals, based on the assumption that polymeric arrays of neutral radicals such as dithiadiazolyls may provide conducting materials. The chemistry of such materials is still expanding rapidly. A comprehensive review on dithiadiazolium and dithiadiazolyl rings by Banister and co-workers [58] covers all known literature till 1995, and only the most recent advances are reviewed here.



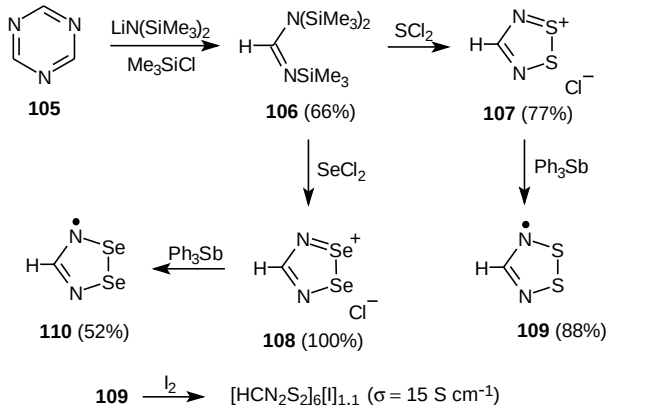
Scheme 26

The radicals associated in the solid state in one of three modes, *i.e.* **100** (R = Ph), **101** (R = C_6H_4CN-*m*), and **102** (R = CF_3, NMe_2, Me) [58–59]. Bisdithiadiazolyls **103** [57] and **104** [59] or the trisdithiadiazolyl **99** [57] are also paramagnetic dimers in the solid state.



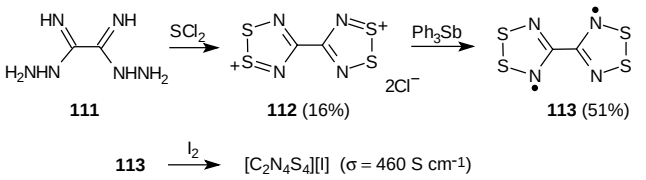
Scheme 27

The parent 1,2,3,5-dithiadiazolium **107** and diselenadiazolium **108** salts have been prepared by reaction of *N*,*N*,*N*'-tris(trimethylsilyl)formamidine **106** (obtained from 1,3,5-triazine **105**) and SCl_2 or $SeCl_2$ (prepared *in situ* from Se and $SeCl_4$) [60]. The corresponding radicals **109**, **110** have also been obtained. Both are dimers of type **100** in the solid state. Cosublimation of the radical **109** in the presence of iodine yielded an iodine-doped hexagonal phase of composition $[HCN_2S_2]_6[I]_{1.1}$ whose single crystal conductivity was 15 S cm^{-1} at room temperature [61].



Scheme 28

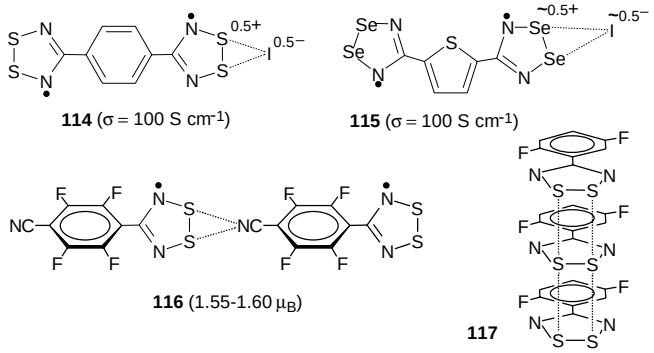
Similarly, the reaction of oxamidrazone **111** with sulfur dichloride afforded 4,4'-bis(1,2,3,5-dithiadiazolium) dichloride **112**, which could be reduced with triphenylantimony to the corresponding bis(1,2,3,5-dithiazolyl) diradical **113**. In the solid state the diradical **113** was a dimer. Cosublimation of the diradical **113** with iodine produced a charge-transfer crystalline salt, in which the heterocyclic rings formed perfectly superimposed stacks, with a single crystal conductivity of 460 S cm^{-1} at 300 °K [62].



Scheme 29

The conductivity in charge transfer salts of dithiadiazolyls is a consequence of two effects; first, the half-filled energy bands from one-dimensional stacks of π–radicals, and second, the electron transfer effect between cation and anion [63]. Cosublimation with iodine of dithiadiazolyls is a good method to obtain conducting charge transfer salts in which the metallic state is stabilized by *p*-type doping of the energy band away from the half-filled level associated with the neutral π-radicals. For example, the 1:1 charge transfer salts of iodine cosublimed with 1,4-phenylene-bis(dithiadiazolyl) diradical **114** [63], and the corresponding to 2,5-thiophene bridged bis(1,2,3,5-diselenadiazolyl) **115** [64], reached a conductivity of 100 S cm^{-1} at room temperature.

In addition to the conducting properties, there has been considerable interest in the magnetic behavior of dithiadiazolyls. The solid structure of the fluorinated 1,2,3,5-dithiadiazolyl radical **116** was reported to be built

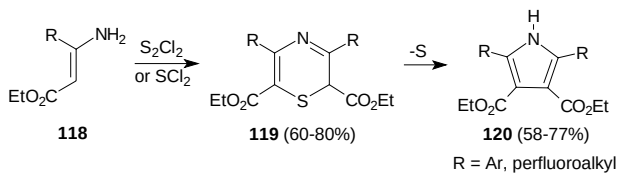


Scheme 30

up of discrete radicals with close contacts between the sulfur–sulfur bridge and the cyano group of another molecule, therefore being the first dithiadiazolyl radical to retain its paramagnetic character in the solid state [65]. It could be prepared as either of two polymorphs, the α-phase having an effective magnetic moment of 1.60 μ_B. The β-phase also consisted of discrete monomeric dithiadiazolyl radicals, and had an effective magnetic moment of 1.55 μ_B at room temperature. Compound **116** showed weak ferromagnetism at 36 K, being the first organic radical to exhibit spontaneous magnetization above liquid helium temperature [65]. Recently, the first undoped dithiadiazolyl radical **117**, which formed a uniform stack in the solid state, preventing the formation of the expected dimers, has been reported [66]. Despite the long *S···S* contacts in **117**, it was a diamagnetic solid, and therefore it could be concluded that longer distances between dithiadiazolyls in **117** are needed to induce paramagnetic behaviour.

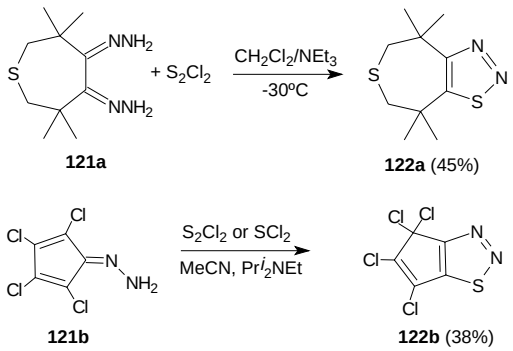
4. Heterocycles from Disulfur Dichloride and Nitrogen Containing Reagents

Disulfur dichloride, S_2Cl_2, a common reagent of the sulfur halides series [67], can be considered one of the best sulfur transfer reagents in heterocyclic synthesis. Its addition to activated double bonds formed heterocyclic compounds, as for example 1,4-thiazines **119** or pyrroles **120** from 3-aminoacrylates **118** [68].



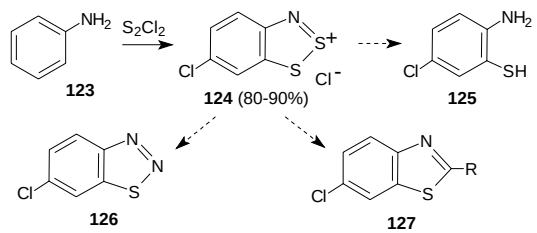
Scheme 31

It is also able to react with carbon–nitrogen double or triple bonds giving notable reactions frequently used for the synthesis of heterocycles, as the 1,2,3-thiadiazoles **122a**,**b** from hydrazones **121a**,**b** [69–70]. Some of these sulfur additions to give heterocycles with one sulfur atom are also performed by the related reagent, sulfur dichloride.



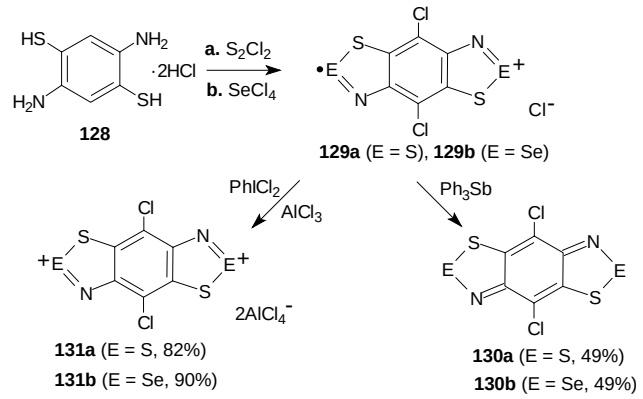
Scheme 32

The most remarkable reactions are those that imply addition of the two sulfur atoms to carbon and nitrogen atoms, giving rise to 1,2,3-dithiazole derivatives. The oldest and best-known reaction of this series is the Herz reaction [71], in which aniline **123** was converted into a 1,2,3-benzodithiazolium salt **124**, very useful as an intermediate for the synthesis of 2-aminothiophenols **125** and some heterocycles (*i.e.* **126** and **127**). Heteroaromatic primary amines reacted in a similar fashion.



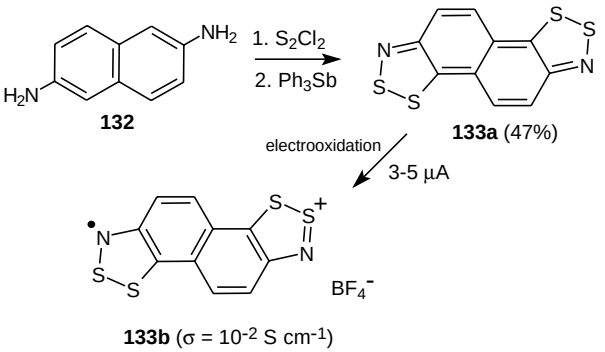
Scheme 33

The reverse reaction, conversion of 2-aminothiophenol into 1,2,3-benzodithiazolium salt was also possible. In a recent application the condensation of diaminobenzenedithiol **128** with disulfur dichloride afforded the chloride salt of the radical cation **129a** which could be reduced to neutral dichlorobenzobis(1,2,3-dithiazole) **130a** with triphenylantimony. A similar condensation with selenium tetrachloride gave **129b** that, upon reduction, yielded the corresponding bis(1,2,3-thiaselenazole) **130b**. Both compounds **130a**,**b**, which are formally antiaromatic 16π-systems, exhibited bond lengths consistent with a quinoid formulation. Dications **131a**,**b** were obtained by oxidation of the radical cations **129a**,**b** [72].



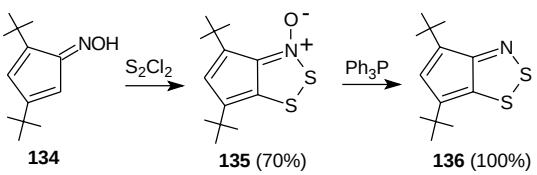
Scheme 34

A double Herz condensation of 2,6-diaminonaphthalene **132** with S_2Cl_2 was recently used to obtain naphthobis(1,2,3-dithiazole) **133a** which was electrooxidized to the conducting π–stacked mixed valence salt **133b** [73].



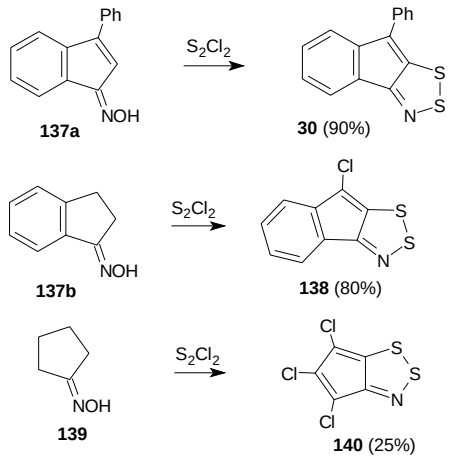
Scheme 35

The addition of disulfur dichloride to both nitrogen and carbon of other suitable precursors permitted the preparation of 1,2,3-dithiazole derivatives. For example, the sterically protected cyclopentadiene oxime **134** was converted into the cyclopenta-1,2,3-dithiazole *N*-oxide **135** by S_2Cl_2 [74]. The *N*-oxide was reduced by triphenylphosphine to the dithiazole **136**, a violet liquid, sensitive to air and moisture.



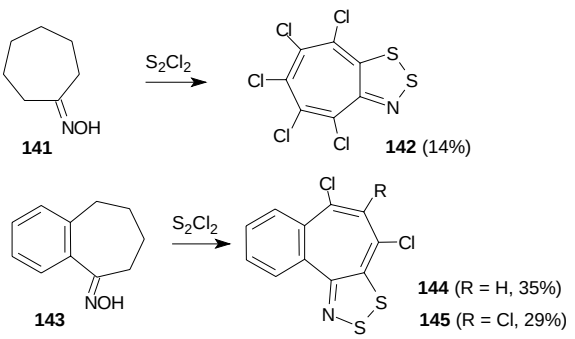
Scheme 36

A rather complex approach to the synthesis of cyclopentadithiazoles was the sequence outlined in Scheme 9 that afforded indeno-1,2,3-dithiazole **30** [23]. Using a much faster approach, the same dithiazole **30** was obtained in one-step reaction from 3-phenylindene-1-oxime **137a** and disulfur dichloride in the presence of *N*-ethyldiisopropylamine [75]. By using this method, protection of the cyclopentadiene ring was not necessary. Cyclopentanone oximes **137b** and **139** afforded respectively 4-chloroindeno-1,2,3-dithiazole **138** and trichlorocyclopenta-1,2,3-dithiazole **140**. The same compounds **138** and **140** were also obtained from the corresponding unsaturated oximes [75].



Scheme 37

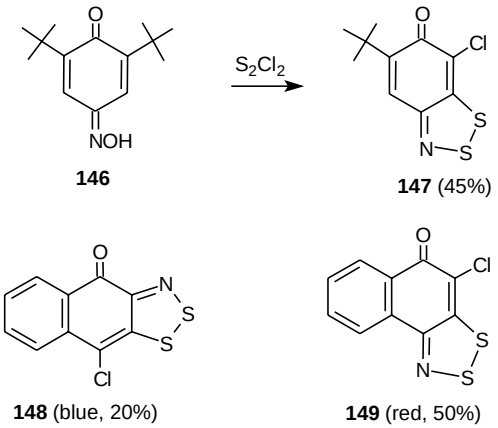
The extensive oxidation and chlorination sequence accompanying the reaction of cyclopentanone oxime with S_2Cl_2 could be extended to the cycloheptanone oxime to give the cyclohepta-1,2,3-dithiazole ring system, a potentially 12π antiaromatic species. In this case the presence of *N*-chlorosuccinimide (NCS) was necessary to complete the formation of the final product. In this way, pentachlorocyclohepta-1,2,3-dithiazole **142** was obtained from cycloheptanone oxime **141** in a one-pot reaction [75]. In the same way, dichoro- **144** or



Scheme 38

trichlorobenzocyclohepta-1,2,3-dithiazole **145** were alternatively obtained from benzosuberone oxime **143** by performing the reaction in the presence or absence of NCS [75].

Disulfur dichloride converted 3,5-disubstituted *p*-benzoquinone monoximes into benzodithiazolones [76]. The benzodithiazolone **147** was obtained from 2,6-di-*tert*-butyl-*p*-benzoquinone-4-oxime **146** as the only product, by substitution of a *tert*-butyl group by chlorine. The isomeric naphthodithiazoles, dark blue **148** and red **149**, were obtained by the same method, starting from *ortho*- and *para*-naphthoquinone monoximes, respectively [76].

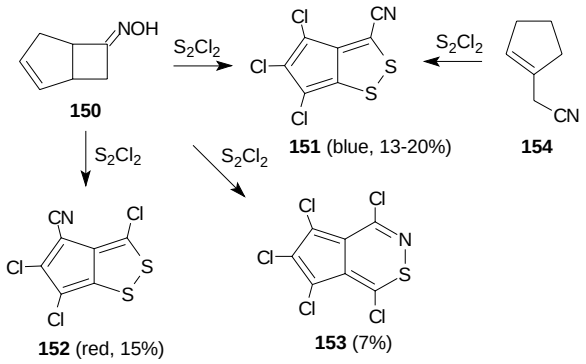


146 **147** (45%) **148** (blue, 20%) **149** (red, 50%)

Scheme 39

The chemistry of disulfur dichloride is not restricted to the synthesis of dithiazoles. The sum of the above mentioned processes (ring formation + aromatization + chlorination) can be combined with other processes, as for example the opening of a cyclobutane ring, to provide other heterocycles. Thus, the reaction of the bicyclic oxime **150** with disulfur dichloride and *N*-ethyldiisopropylamine, gave rise to a new synthesis of heterocyclic pseudoazulenes, cyclopenta-1,2-dithioles, cyclopenta-1,2-thiazines and their benzoderivatives, obtained through a new rearrangement process related to the Beckmann 2nd order, or abnormal, opening of oximes. By the combined oxime rearrangement, disulfur dichloride addition, aromatization and chlorination processes, all in a one-pot reaction, the bicyclic oxime **150** afforded, alternatively, as the main product, the dark blue pseudoazulene **151** or the red **152**, always accompanied by the orange pseudoazulene **153** [77]. The initial opening reaction of the cyclobutane ring that gave rise to **151** was established by the independent synthesis of **151** from cyclopentenylacetonitrile **154** [77].

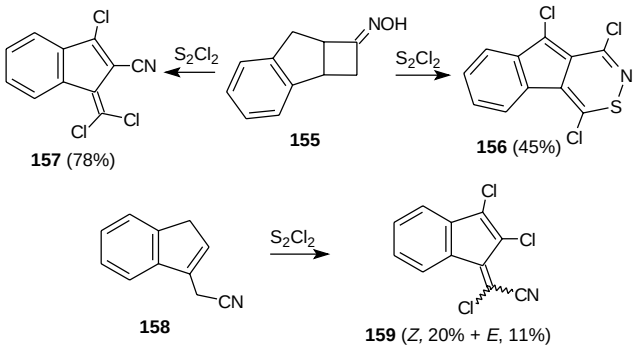
By a similar reaction, tricyclic oxime **155** afforded alternatively, as the main product, pseudoazulene **156** or the indenonitrile **157**. To establish the structure of



150 **151** (blue, 13-20%) **154** **152** (red, 15%) **153** (7%)

Scheme 40

compound **157**, the reaction of indenonitrile **158** and disulfur dichloride was performed, from which compound **159** was obtained, and separated as the *Z* and *E* isomers. The isomers **159** (*Z* and *E*) were also found, from spectroscopic studies, to be isomers of compound **157** [77].



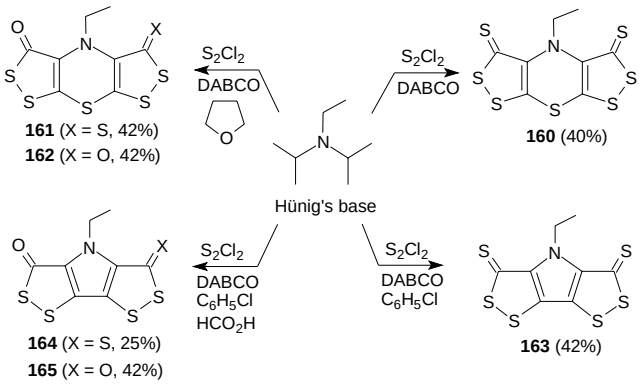
157 (78%) **155** **156** (45%) **158** **159** (*Z*, 20% + *E*, 11%)

Scheme 41

Compounds **151**, **156**, **157**, **159**(*Z*) and **159**(*E*) were the first members of a new class of discotic liquid crystals, in which the mesophases are supported by intermolecular interactions [78]. On heating, all compounds formed columnar mesophases of hexagonal symmetry, confirmed by differential scanning calorimetry and X-ray diffraction of the liquid crystal mesophases.

In a very different reaction, *N*-ethyldiisopropylamine, usually employed as an inert base, reacted with disulfur dichloride to give bis[1,2]dithiolo[1,4]thiazine derivatives [79]. In fact, this base did not react when mixed with S_2Cl_2 during several days at temperatures up to 4 °C, but higher temperatures promoted a slow sulfuration process of the base, affording a variety of heterocyclic compounds in surprisingly good yields. Modification of solvent, refluxing temperature and time, and addition of a stronger base or an oxygen donor, permitted the selective synthesis of each one of the formed products. The treatment of Hünig's base with S_2Cl_2 and

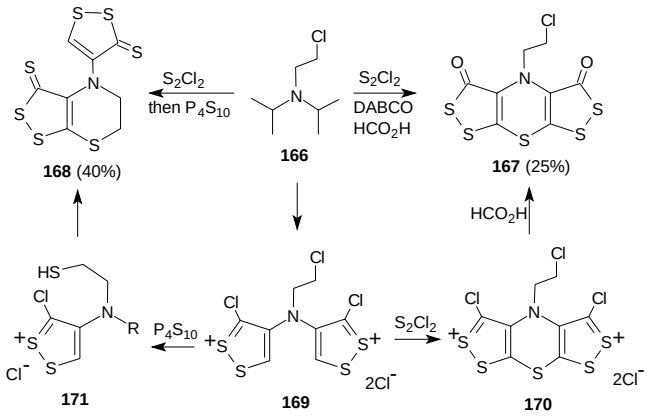
1,4-diazabicyclo[2.2.2]octane (DABCO) for 3 days at room temperature, followed by refluxing for 2 h promotes selectively the complete sulfuration of all the C-H bonds of the two isopropyl groups, converting the initial Et(*i*-Pr)$_2$N into EtNC$_6$S$_7$ and affording the dithione **160**. By variation of the solvent, time of reflux and addition of a source of oxygen, the reaction could be modified to give derivatives of the bis-dithiolothiazine ring system in which one or two exocyclic sulfur atoms were replaced by oxygen. In this way, the oxothione **161** or the dione **162** were selectively obtained [79]. These compounds underwent selective thermal extrusion of the thiazine sulfur atom to give bis[1,2]dithiolopyrroles [80]. Furthermore, the combined Hünig's base reaction and desulfurization allowed the one-pot preparation of pyrrole derivatives **163**, **164** and **165** from Hünig's base [80].



Scheme 42

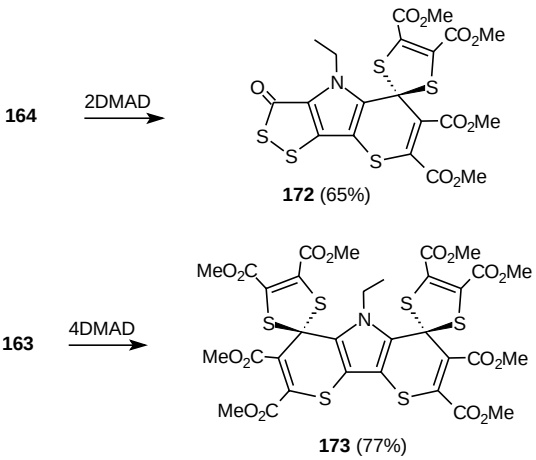
Functionalized ethyl groups may take part into the process. The reaction of *N*-(2-chloroethyl)diisopropylamine **166** with S_2Cl_2, DABCO and formic acid gave the expected product **167** [81]. Nevertheless, addition of phosphorus pentasulfide at a late stage in the reaction formed a thiol derivative from the chloroethyl chain, affording the [1,2]dithiolo[1,4]thiazine derivative **168** [81]. If the reaction started as in previous cases, by forming intermediate salts, the expected intermediate salt **169** may react with S_2Cl_2 to give the tricyclic salt **170** that, by reaction with formic acid, yielded **167**. Alternatively, the salt **169** may, in this case, react with P_4S_{10} to give the thiol **171** that subsequently cyclised to afford the 1,4-thiazine **168**.

Treatment of oxothione **164** with dimethyl acetylenedicarboxylate (DMAD) afforded the spiro[1,3-dithiolethiopyran] **172** as the only product [80]. Two DMAD molecules added to the 1,2-dithiolo-3-thione moiety, leaving the 1,2-dithiolo-3-one ring intact. In an analogous manner, reaction of dithione **163** with excess DMAD afforded the 1:4 adduct, bis-spiro[1,3-dithiolethiopyran]pyrrole **173** with a symmetrical structure [80].



Scheme 43

This fully substituted pentacyclic molecule was obtained from commercial Hünig's base in only two steps, in 32% overall yield.



Scheme 44

The limits of this chemistry are difficult to foresee. Some areas are now currently under intense research, especially those relating to new materials chemistry. The interesting characteristics found in many of the heterocycles, the development of rapid synthetic methods from easily available materials, and the very wide range of products obtainable by these methods offer wide scope for the synthesis of new poly-sulfur-nitrogen heterocycles.

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