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Sulfur monochloride in organic synthesis

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The data on the reactivity of sulfur monochloride published in the past 15 years have been reviewed and systematized. The review focuses on the synthesis of acyclic and heterocyclic compounds with the use of S_2Cl_2.
The bibliography includes 154 references.

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I. Introduction

Sulfur-containing organic compounds have attracted special attention of scientific community for several centuries of the development of chemical science. This is due to the fact that sulfur is one of the chemical elements that play a crucial role in the life of plants and animals, including humans. In addition, in recent years, compounds containing sulfur atom(s) have been used for designing promising materials for various fields of science and technology. The synthesis of target sulfur-containing compounds often requires a large number of steps and the use of expensive starting reagents. Despite the fact that many methods are currently available for introducing sulfur atoms into organic molecules (for example, with the use of elemental sulfur, sulfur pentachloride, Lawesson's reagent, *etc.*),[1] they are not always suitable for the introduction of a certain number of atoms.

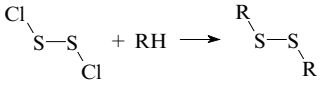
Sulfur chlorides (S_nCl_2) containing two chlorine atoms at the ends of a polymeric chain of sulfur atoms can be treated as promising reagents for the solution of this synthetic problem. Many of them ($n = 1-12$) are known, some of them have been isolated, but only two of them — sulfur dichloride (SCl_2) and sulfur monochloride (S_2Cl_2) — are commercially available chemicals. Sulfur dichloride is unstable, and it should be distilled immediately before use. Sulfur monochloride is rather stable and can be stored in dark glass bottles for months, even years, slightly decomposing into sulfur dichloride and elemental sulfur.[2]

According to the IUPAC nomenclature, the S_2Cl_2 compound is named disulfur dichloride. However, we will use a more harmonic, in our opinion, name — sulfur monochloride. This compound has been so named since its discovery, when only the ratio of the sulfur and chlorine atoms in the molecule was determined. Both names are equally used in the modern literature.

A specific feature of sulfur monochloride is its diverse reactivity. It is a strong chlorinating agent, but is rarely used as such since there are many other chlorinating agents that afford higher yields of reaction products. The oxidative ability of S_2Cl_2 has been studied to a much lower extent. This is due to the fact that the products of formal oxidation reactions are formed, as a rule, in the course of complex multistage processes involving chlorination, dehydrochlorination, sulfuration, *etc.*

The most useful property of this compound is believed to be its sulfurating ability. A striking example of this kind of transformations is the well-known Herz reaction (the reaction of S_2Cl_2 with aromatic amines). However, sulfuration reactions are often accompanied by undesirable chlorination. Numerous attempts have been undertaken to use analogous sulfurating agents with carbon-, nitrogen-, oxygen-, sulfur- and silicon-containing groups instead of chlorine atoms (Scheme 1, synthesis of similar compounds will be considered below), but these disulfides turned out to be much less efficient. Until now, sulfur monochloride remains one of the best sulfurating reagents in both inorganic and organic chemistry.

Scheme 1



R = Ar, $NAlk_2$, OAlk, SAlk, SiAlk

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In the late 1990s and early 2000s, several reviews were published dealing with the synthesis of sulfur-containing heterocycles with the use of sulfur chlorides.[3–5] However, they do not cover all aspects of the reactivity and synthetic potential of sulfur monochloride. In 2008, we wrote a chapter in the monograph *Advances in Heterocyclic Chemistry*[6] where the synthesis of heterocyclic compounds with the use of S_2Cl_2 has been presented. Since the time of this publication, many new data on this topic have accumulated. In addition, no reviews are available that summarize data on the use of sulfur monochloride in synthesis of acyclic derivatives. Therefore, we believe it is appropriate to consider studies dealing with the use of S_2Cl_2 in organic synthesis published over the past 15 years.

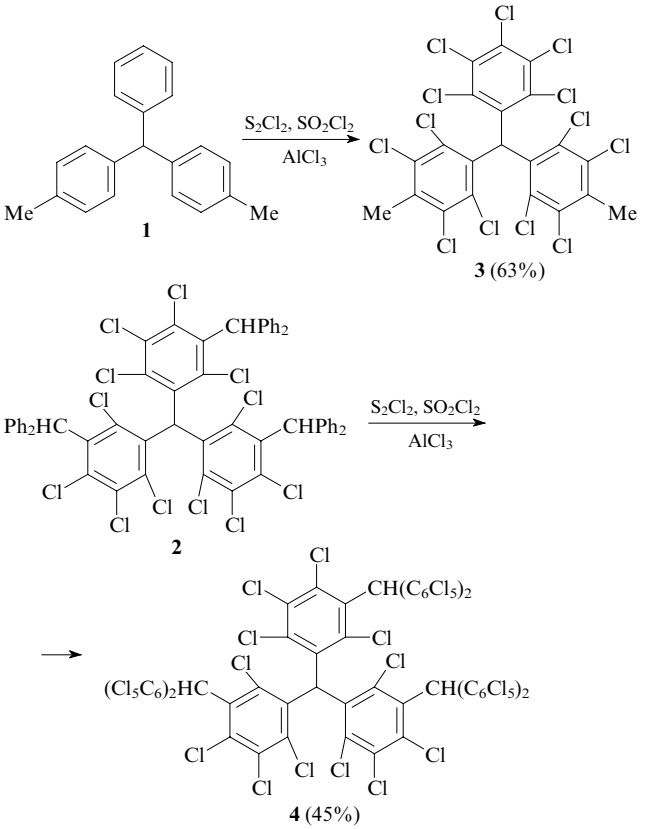
II. Synthesis of acyclic compounds

1. Sulfur-free compounds

a. Chlorination of (het)arenes

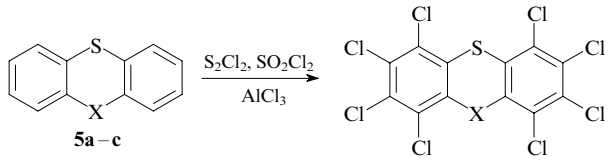
Chlorination of aromatic compounds with sulfur monochloride in sulfuryl chloride catalyzed by aluminium chloride was accomplished for the first time for benzene derivatives (toluene, *p*-xylene and mesitylene).[7] Recently, this reaction has been successfully applied to polycyclic compounds. In particular, triphenylmethane derivatives **1** and **2** under such conditions are converted into perchlorinated compounds **3** and **4** (Scheme 2). Although the yields are moderate, it is worth noting that, respectively, 13 and 30 chlorine atoms are introduced at a time into a molecule.[8,9]

Scheme 2



The use of this reagent system for thianthrene (**5a**), phenoxathiin (**5b**) and 4a,9b-dihydrodibenzothiophene (**5c**) leads to the exhaustive chlorination of these compounds to form perchlorinated products **6a**–**6c** in quantitative yield (Scheme 3).[10]

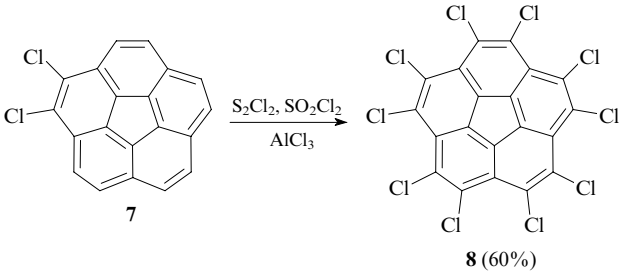
Scheme 3



X = S (**a**), O (**b**), absent (**c**)

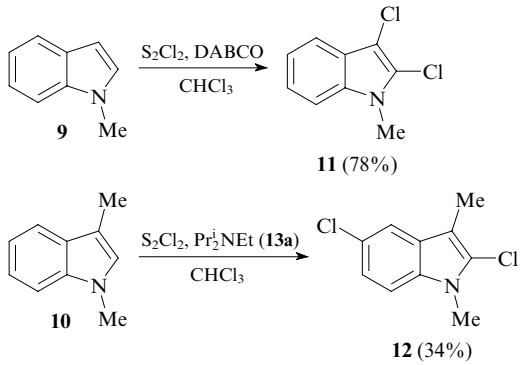
Analogous results have also been obtained for 2,3-dichlorocorannulene (**7**): the yield of perchlorinated polycycle **8** is 60% (Scheme 4).[11]

Scheme 4



Indole derivatives — 1-methylindole (**9**) and 1,3-dimethylindole (**10**) — are chlorinated under much milder conditions (Scheme 5). In both cases, two chlorine atoms are introduced into the molecule: into the pyrrole ring in the first reaction (compound **11**),[12] and when one of the positions of the pyrrole ring has been occupied by methyl group, into the pyrrole and benzene rings in the second reaction (compound **12**).[13] As bases, 1,4-diazabicyclo[2.2.2]octane (DABCO) and diisopropylethylamine (**13a**, Hunig's base) have been used.

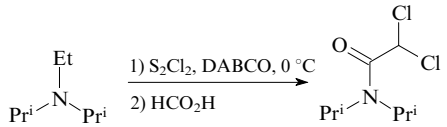
Scheme 5



b. Conversion of *N*-ethylamines into amide derivatives

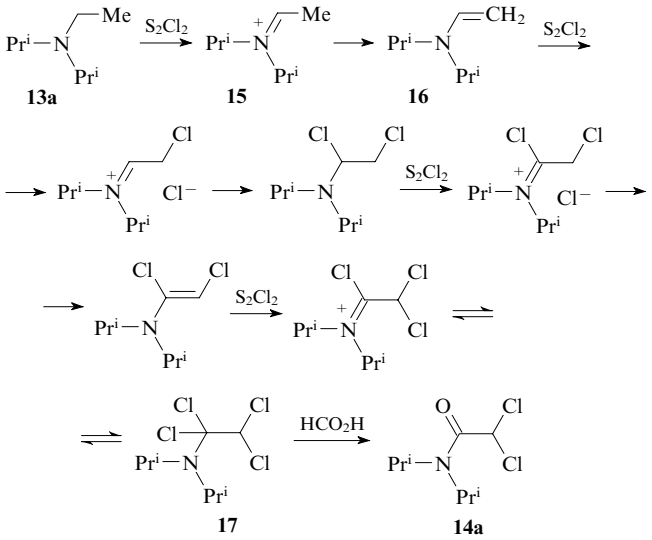
It has long been believed that only isopropyl groups are involved in the reaction of diisopropylethylamine (**13a**) with sulfur monochloride. However, it was shown in 2001[14] that the reaction pathway radically changes at low temperature (0 °C) in the presence of DABCO. The *N*-ethyl group is selectively involved in the reaction, and treatment with formic acid leads to *N*,*N*-diisopropyl(dichloroacetamide) (**14a**) with intact isopropyl groups (Scheme 6).

Scheme 6



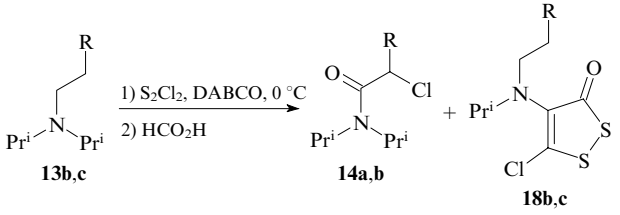
The key stage of the process is, presumably, the oxidation of a tertiary amine with sulfur monochloride to iminium ion **15**, which can isomerize to give enamine **16**. The latter is oxidized to form tetrachlorinated derivative **17**, which reacts with formic acid to give target amide **14a** (Scheme 7).

Scheme 7



Conversion of the *N*-ethyl group into the dichloroacetamide one offers new possibilities for functionalization of *N*-alkyl groups. Further studies of reactions of N-substituted diisopropylamines with S_2Cl_2 in the presence of DABCO have shown that reaction products essentially depend on the nature of substituent R (Scheme 8).[15] In particular, the reaction of diisopropyl-2-chloroethylamine (**13b**) with S_2Cl_2 and DABCO at 0 °C with subsequent treatment with formic acid leads to dichloroacetyl derivative **14a**; however, the major product is 5-chloro-1,2-dithiol-3-one **18b**. It is evident that the chloroethyl group in amine **13b** is oxidized like the ethyl one, but much more slowly so that the competing reaction involving the isopropyl group occurs to give dithiolone **18b**.

Scheme 8

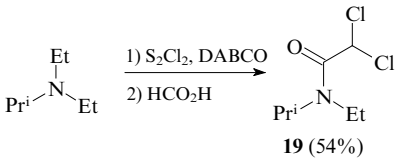


Compound		R	Yield (%)	
14	**13**, **18**		**14**	**18**
a	**b**	Cl	21	34
b	**c**	phthalimido (Phth)	22	33

Diisopropyl(2-phthalimidoethyl)amine (**13c**) reacts under these conditions analogously to chloro derivative **13b** to give, respectively, chloroacetamide **14b** and dithiolone **18c** in nearly the same yields.

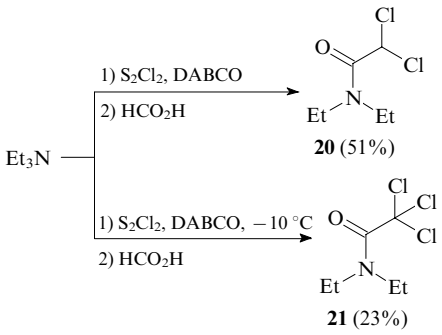
Study of the same reaction with isopropyldiethylamine and triethylamine has demonstrated that, as expected, the yields of dichloroacetyl derivatives increase.[15] In particular, isopropyldiethylamine forms at 0 °C dichloroacetamide **19** in 34% yield. Even if the reaction is carried out at room temperature for three days, only the ethyl group is subjected to transformation; the yield of acetamide **19** increases to 54% (Scheme 9).

Scheme 9



Optimal temperature for the reaction of S_2Cl_2 and DABCO with triethylamine (without isopropyl groups) is also room temperature: the yield of dichloroacetamide **20** is 51%. However, when the reaction is carried out at 10 °C, amide **20** is formed in trace amounts, while the major product is trichloroacetyl derivative **21** (23%). Formation of trichloroacetamide **21** upon the chlorination of the ethyl group in triethylamine has been attributed to the decrease in steric hindrances in the substrate as compared with Hunig's base and isopropyldiethylamine (Scheme 10).

Scheme 10

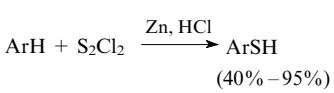


2. Compounds with one sulfur atom

a. Thiophenols

A classical method of synthesis of substituted thiophenols is the reaction of aromatic compounds with sulfur monochloride followed by the reduction of the resulting diaryl sulfides with zinc in hydrochloric acid. Recently, this method has been actively used for preparing target products. To avoid the formation of a mixture of isomeric thiophenols, it is necessary to use compounds in which one of the positions is significantly more activated toward the electrophilic attack than the other positions (Scheme 11).[16–19]

Scheme 11



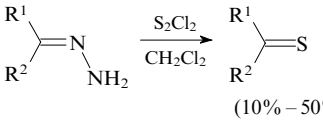
Ar = 3,5-Bu^t_2-4-$MeOC_6H_2$, 2,4-Bu^t_2-6-$(C_6F_5NH)C_6H_2$, *etc.*

As catalysts for synthesis of diaryl disulfides, titanium tetrachloride [17] or iron powder [19] are used. No correlation has been revealed between the yields and reaction conditions or catalysts used.

b. Thioketones

Despite the fact that the reaction of disubstituted hydrazones with sulfur monochloride was discovered more than thirty years ago,[20] it has been comprehensively studied in recent years with the aim of synthesizing different polysulfur-containing heterocycles (see below). However, only thioketones have been isolated as major products, their yield being as high as 50% (Scheme 12).[21,22]

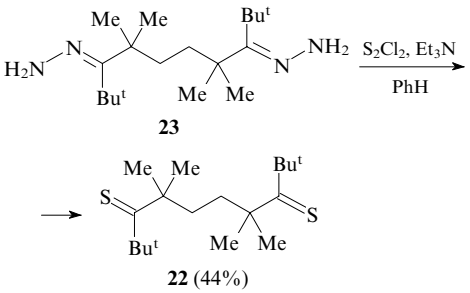
Scheme 12



R^1 = Bu^t, Ph, Ad; R^2 = Bu^t, Ph; Ad is 1-adamantyl

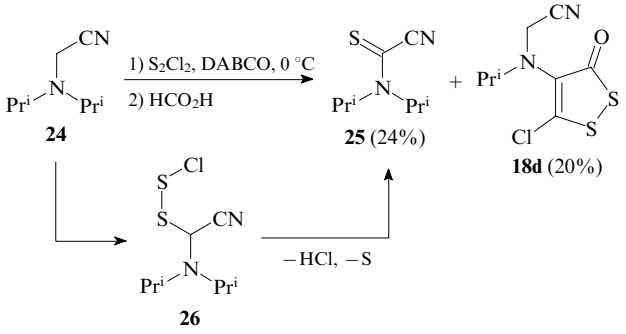
It has been later shown [23] that bis(thioketone) **22** can be obtained by the reaction of dihydrazone **23** with sulfur monochloride in the presence of triethylamine, although the yield of the product turned out to be low — 44% (Scheme 13).

Scheme 13



The possibility of the direct transformation of the methylene group to the thioketone group under the action of sulfur monochloride has been proved for diisopropyl(2-cyanoethyl)amine (**24**) as an example.[15] The yield of cyanothioformyl derivative **25** was 24%, since the reaction was complicated by the formation of dithiolone **18d** — the product of the competing reaction involving one of the isopropyl groups. The authors suggest that, in this case, S_2Cl_2 is attached to the activated methylene group to give derivative **26** and then atomic sulfur and HCl molecule are removed (Scheme 14).

Scheme 14



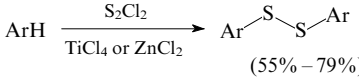
3. Compounds with two sulfur atoms

The introduction of two sulfur atoms through the reaction with sulfur monochloride in an organic molecule accompanied by removal of two HCl molecules is the most important and widely used process involving this reagent.

a. Di(het)aryl disulfides

Synthesis of diaryl disulfides from arenes and sulfur monochloride requires, as a rule, the presence of Lewis acid as a catalyst. The best results have been achieved when titanium tetrachloride [24] or zinc chloride [25] are used. To avoid the formation of isomers, aromatic compounds containing bulky substituents [isopropyl, *tert*-butyl, phenyl(methyl)-ethyl and other groups] are usually introduced into the reaction (Scheme 15).

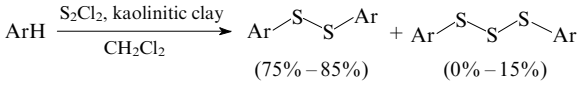
Scheme 15



Ar = 2,4,6-Pr$^i_3$C$_6$H$_2$, 2,6-Me$_2$-4-Bu^{t}C$_6$H$_2$, 3,5-(Me$_2$PhC)$_2$-2-HOC$_6$H$_2$

When kaolinitic clay serves as a heterogeneous catalyst, the yieds of diaryl disulfides increase; however, the reaction gives also diaryl trisulfides in yields up to 15% (Scheme 16).[26]

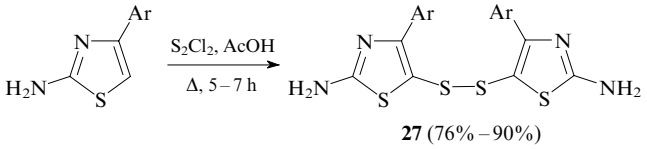
Scheme 16



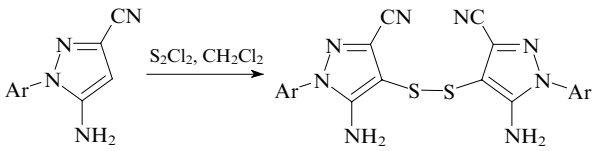
Ar = Ph, 4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$, Naph, *etc.*; Naph is 1-naphthyl

If heteroaromatic thiazole and pyrazole derivative have only one unsubstituted position, their reactions with sulfur monosulfide provide disulfides **27** and **28** in high yields.[27–29] In this case, the reaction can be carried out even in the absence of a catalyst (Scheme 17).

Scheme 17



Ar = 4-BrC$_6$H$_4$, 4-ClC$_6$H$_4$, 3,4-Cl$_2$C$_6$H$_3$, *etc.*

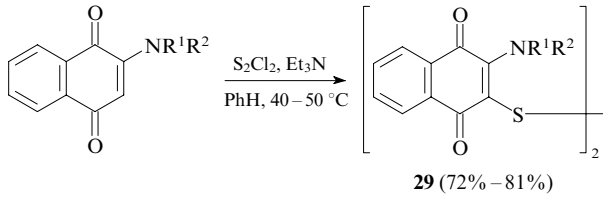


Ar = 4-F$_3$C-2,6-Cl$_2$C$_6$H$_2$, 4-F$_3$C-2-ClC$_6$H$_3$, 4-F$_3$C-4-F-2-ClC$_6$H$_2$

Analogous results have been obtained for 2-aminonaphthoquinones; the reaction conditions and the yields of target **29** are almost independent of the nature and number of substituents in the amino group in vicinal position to the C–H bond (Scheme 18).[30]

In some cases, the reactions of sulfur monochloride with arenes [31] and indoles [13] yield mixtures of RS_nR polysulfides,

Scheme 18



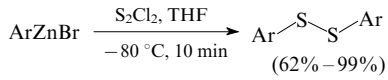
29 (72%–81%)

R^1, R^2 = H, Et, Bu^n, 4-ClC_6H_4, *etc.*

where R = Ar or Het, $n = 1-4$; it is clear that such reactions are of no synthetic value.

Organometallic compounds can be used for obtaining aromatic and heteroaromatic disulfides. For example, some disulfides have been synthesized by the reaction of organozinc derivatives with sulfur monochloride.[32] In synthesis of diferrocenyl disulfides, organolithium compounds have been used as initial reagents.[33] Indubitable advantages of these methods are extremely mild reaction conditions, selectivity and high product yields (Scheme 19).

Scheme 19

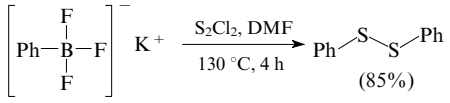


(62%–99%)

Ar = 4-MeC_6H_4, 4-ClC_6H_4, 4-$EtOC_6H_4$, 2-NCC_6H_4, Fc, 5-EtO_2CFu, *etc.*; Fc is ferrocenyl, Fu is 2-furyl

Diphenyl disulfide was synthesized from such an exotic compound as potassium phenyltrifluoroborate, although under rather severe conditions (Scheme 20).[34]

Scheme 20



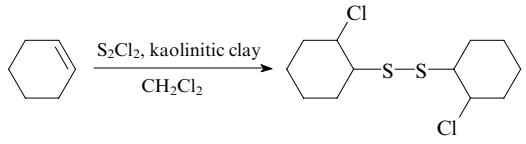
(85%)

b. Aliphatic disulfides

Two types of aliphatic substrates — alkenes and aldehydes — are prone to reaction with sulfur monochloride, leading to disulfides.

In particular, the reaction of cyclohexene with S_2Cl_2 in the presence of a heterogeneous catalyst (kaolinitic clay) leads to 2,2′-dichlorodicyclohexyl disulfides (**30**) in high yield (Scheme 21). As distinct from the reaction with arenes (see previous section), no formation of trisulfides is observed.[26]

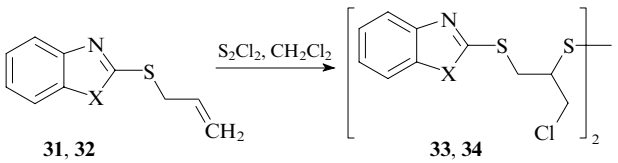
Scheme 21



30 (80%)

2-Allylthiobenzoxazole (**31**) and -benzothiazole (**32**) react with sulfur monochloride to give corresponding disulfides **33** and **34** (Scheme 22).[35] The formation of linear rather than cyclic products is explained by the absence, in the initial compounds, of hydrogen atoms that can be eliminated in the course of reaction with sulfur monochloride.

Scheme 22



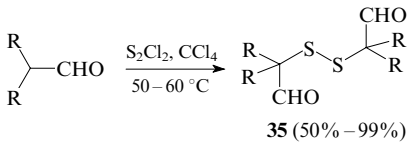
31, **32** **33**, **34**

X = O (**31**, **33**; yield 27%), S (**32**, **34**; 38%)

It should be noted that these two reactions are rare examples of addition of the S_2Cl_2 molecule to the organic substrate.

The reaction of sulfur monochloride with aliphatic aldehydes containing a hydrogen atom in the α-position is a well-known method of synthesis of synthetically valuable 3,4-dithiahexane-1,6-dialdehydes **35**. Usually, an aldehyde and S_2Cl_2 are mixed in carbon tetrachloride, and the reaction mixture is kept at room temperature or at 50–60 °C for several hours. The yields of the products vary from moderate to nearly quantitative (Scheme 23).[36, 37]

Scheme 23



35 (50%–99%)

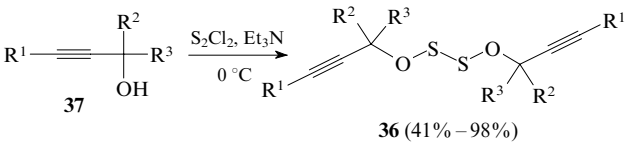
R = Me, Et, Ph, cyclo-C_6H_{11}, *etc.*

c. Dialkoxy disulfides

Dialkoxy disulfides have been known for more than 100 years; however, interest in these compounds is unabated owing to their diverse reactivity. Modern strategy of synthesis of dialkoxy disulfides is based on the method described by Thompson *et al.*[38] These synthetically important compounds are often introduced into further transformations without isolation from the reaction mixture.

Substituted bis(propargyloxy) disulfides **36** have been synthesized by the reaction of propargyl alcohols **37** with sulfur monochloride in the presence of triethylamine in ether or methylene chloride at 0 °C. The yields of the products vary from moderate to nearly quantitative (Scheme 24).[39, 40]

Scheme 24



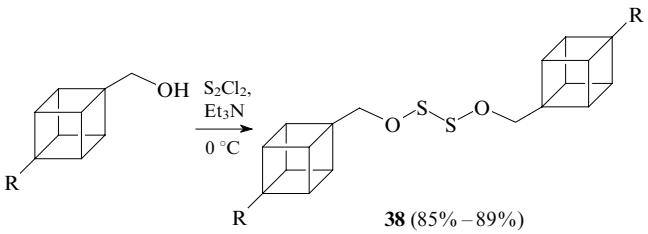
37 **36** (41%–98%)

R^1, R^2, R^3 = H, Me, Et, Pr^i, Bu^i, Bu^t, Bn, *etc.*

Analogous procedures have been successfully applied to synthesis of substituted bis(allyloxy) disulfides,[41] bis(benzyloxy) disulfides[42] and other dialkoxy disulfides,[43] including cubane derivatives **38** (Scheme 25).[44]

In the reaction with propargyl alcohols **39**, intermediate unstable monoalkoxychloro disulfides **40** have been detected; the latter react with 2,3-dimethyl-1,3-butadiene

Scheme 25

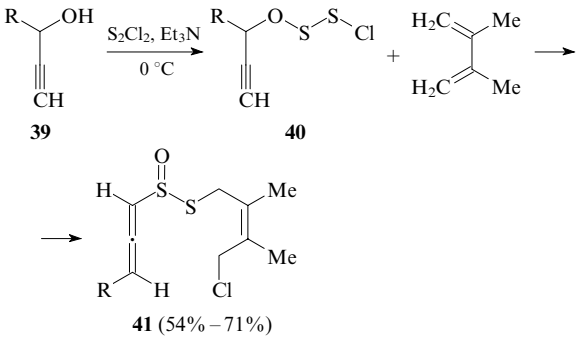


38 (85%–89%)

R = H, I

to give rearrangement products — mixed thiosulfinates **41** (Scheme 26).[45]

Scheme 26



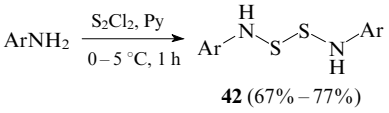
39 **40** **41** (54%–71%)

R = Me, Et, Pr^i, Bu^i, n-C_5H_{11}, neo-C_5H_{11}

d. Bis(amino) disulfides

Reactions of secondary amines with S_2Cl_2 have been studied for a rather long time; however, no serious progress has been achieved in this field in the past 15 years. Among these reactions, the synthesis of bis(arylamino) disulfides **42** from anilines and sulfur monochloride in the presence of pyridine (Py) is noteworthy (Scheme 27).[46]

Scheme 27

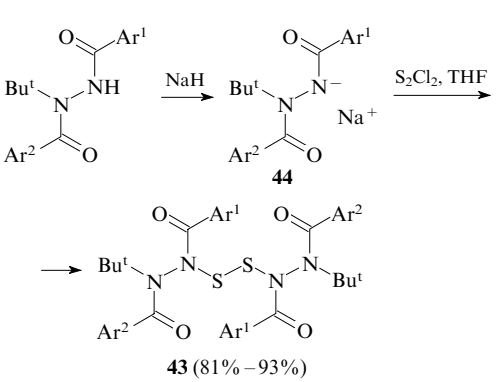


42 (67%–77%)

Ar = 4-$F_3CC_6H_4$, 4-$F_3COC_6H_4$

To obtain *N*-alkyl-*N*′-(dithio)diacylhydrazines **43**, reactions of sulfur monochloride with sodium salts of *N*′-*tert*-butyl-*N*,*N*′-diacylhydrazines **44** have been suggested.[47] As a rule, such disulfides are formed in high yields (Scheme 28).

Scheme 28



44

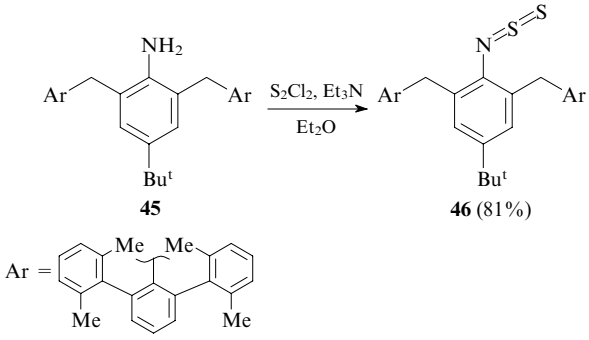
43 (81%–93%)

Ar^1 = Ph, 4-EtC_6H_4, 4-ClC_6H_4; Ar^2 = 3-MeC_6H_4, 3,5-$Me_2C_6H_3$

e. Thiosulfinylanilines

A representative of a rare and extraordinary class of organosulfur compounds — thiosulfinylamines — was synthesized by the reaction of 'cup-shaped' aniline **45** with sulfur monochloride in the presence of triethylamine.[48] The yield of compound **46** was unexpectedly high (81%), and the compound turned out to be stable (Scheme 29).

Scheme 29

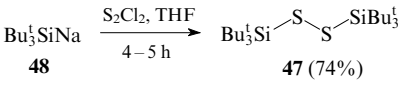


45 **46** (81%)

f. Bis(trialkylsilyl) disulfides

The only example of synthesis of bis(tri-*tert*-butylsilyl) disulfide (**47**) has been described: through the reaction of sodium derivative of tris(*tert*-butyl)silane (**48**) with S_2Cl_2 in tetrahydrofuran (Scheme 30).[49]

Scheme 30

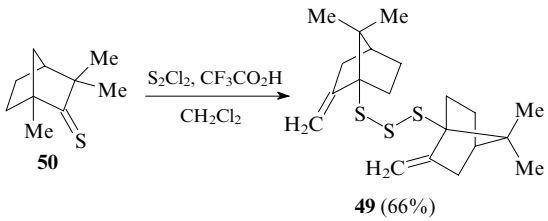


48 **47** (74%)

4. Compounds with three sulfur atoms

As a rule, the reaction of thiols or thioketones with sulfur monochloride leads to compounds containing four sulfur atoms — tetrasulfides (see next Section). However, trisulfide **49** is known to form in the reaction of thioketone **50** with S_2Cl_2 (Scheme 31).[50] The highest yield of the product (66%) has been achieved in the reaction catalyzed by trifluoroacetic acid. It should be noted that neither strong evidence of the structure of trisulfide **49** nor explanations of the mechanism of its formation have been reported.

Scheme 31

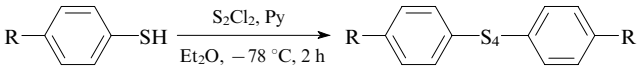


50 **49** (66%)

5. Compounds with four sulfur atoms

Symmetric aromatic tetrasulfides **51** can easily be obtained by the reaction of corresponding thiols **52** with sulfur monochloride.[51] The use of pyridine as a base leads to an increase in the yield of target products (Scheme 32).

Scheme 32

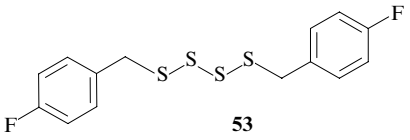


52 **51** (71%–99%)

R = H, Me, Br, NO_2

Bis(4-fluorobenzyl) tetrasulfide (**53**) has been synthesized by the same scheme.[52]

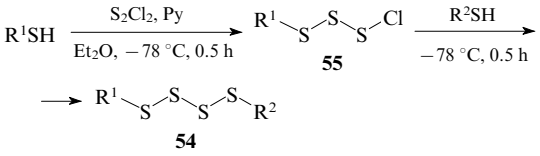
Structure 53



53

On the basis of this reaction, a method of synthesis of asymmetric tetrasulfides **54** has been recently suggested. It consists in the reaction of thiol with one equivalent of sulfur monochloride in the presence of pyridine at −78 °C and subsequent treatment of intermediate trisulfane **55** with another thiol (Scheme 33).[53] The reaction has been carried out with different thiols containing benzyl, aryl and hetaryl moieties. The yields of the products have not been reported.

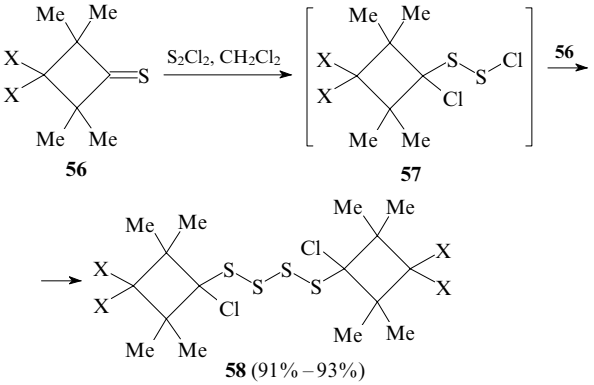
Scheme 33



R^1, R^2 = Ar, Bn, CH_2Ar, CH_2Het

Four-membered thioketones **56** readily add to sulfur monochloride to form chlorodithio derivative **57**. The latter is too unstable to be isolated as an individual compound. However, such an intermediate can further react with a second molecule of thioketone **56** to form tetrasulfane **58** (Scheme 34).[54, 55]

Scheme 34

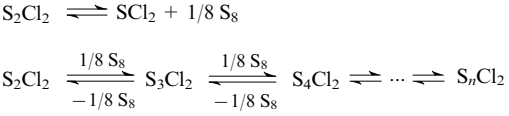


2X = O, X = Cl

III. Synthesis of heterocyclic compounds

The most important property of sulfur monochloride is believed to be its ability to cyclize different organic substrates. Taking into account the structure of the S_2Cl_2 molecule, one can suggest that the most frequently encountered pathway of such reactions should be the insertion of two sulfur atoms between two carbon atoms or between carbon and nitrogen atoms. However, in some cases, S_2Cl_2 enables the introduction of one sulfur atom, as well as several S atoms — three, four, five and even ten, and these atoms can be either bonded or not bonded to one another. Such reactions cannot be explained only by disproportionation of sulfur monochloride into sulfur dichloride and sulfur and subsequent formation of higher sulfur chlorides, as was attempted by Harpp *et al.*[56] in 1978 (Scheme 35). As shown by recent stidies, S_2Cl_2 plays a decisive role in all transformations.

Scheme 35



In 2009, we suggested a classification of cyclization reactions of organic substrates under the action of sulfur monochloride.[57] The classification is based on the fact that the result of these transformations, namely, the type of resulting heterocycle and the number of sulfur atoms introduced into it, depends on the number of carbon and nitrogen atoms in the moiety of the initial molecule involved in the formation of the product; the decisive factor for successful reaction is the stability of the new heterocycle. Analysis of the literature data demonstrates that nearly all reactions that have been studied previously and during the time elapsed from the publication of our paper [57] perfectly fit into this classification. However, for simplicity of perception of necessary information, we decided to use the same principle of systematization in the second part of the review as in the first part, *i.e.*, systematization based on the number of sulfur atoms in the resulting heterocyclic compound.

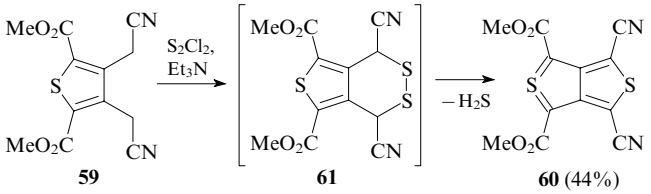
1. Heterocycles with one introduced sulfur atom

The cyclization of an organic substrate with participation of sulfur monochloride often leads to the introduction of only one sulfur atom into the resulting heterocycle. Such reactions usually imply removal of the sulfur dichloride (SCl_2) molecule or atomic sulfur from the intermediate compound, which is accompanied by contraction of the ring to a more stable (as a rule, heteroaromatic) compound.

a. Thiophenes

One of the initial fragments most widely used for formation of the thiophene ring is represented by two activated methylene groups in appropriate positions. For example, 3,4-di(cyanomethyl)-2,5-di(methoxycarbonyl)thiophene (**59**) reacts with sulfur monochloride to give tetrasubstituted

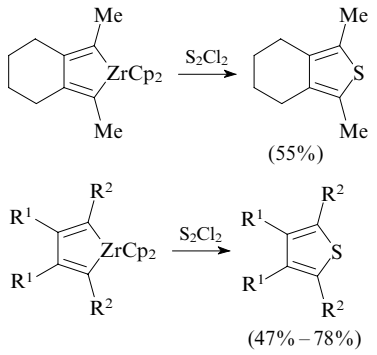
Scheme 36



thieno[3,4-*c*]thiophene **60** in moderate yield.[58] In the suggested mechanism of formation of thiophene **60**, the intermediate product is compound **61**. It has been demonstrated that the use of S_2Cl_2 ensures higher yield of the product than in the case of SCl_2 (10%), and at the last stage, sulfur monochloride acts as an oxidant (Scheme 36).

Recently, zirconium metallocenes have been often used for formation of the thiophene ring with participation of sulfur monochloride;[59] this procedure has been applied to synthesize thiophene as shown in Scheme 37.[59–61]

Scheme 37

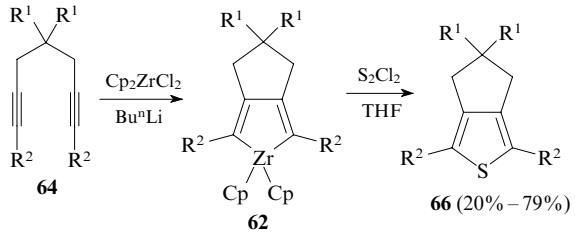


R^1 = Et, Pr^n, Bu^n, Ph, C_6F_5; R^2 = Et, Pr^n, Bu^n, Ph, $SiMe_2Alk$; Cp is cyclopentadienyl

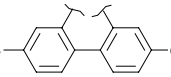
In these cases, sulfur monochloride provides higher yields of thiophene as compared with sulfur dichloride, although only one sulfur atom is introduced into the molecule. The reaction conditions are usually mild: the reactants are kept at room temperature for several hours, and the yields of target products vary from moderate to high.

Zirconocenes **62** and **63** can be synthesized from diynes **64** and **65** by the reaction with the Negishi reagent, which is obtained from bis(cyclopentadienyl)zirconium dichloride and two equivalents of n-butyllithium. Subsequent treatment of compounds **62** and **63** with sulfur monochloride yields thiophenes **66** and **67** (Scheme 38).[62–64]

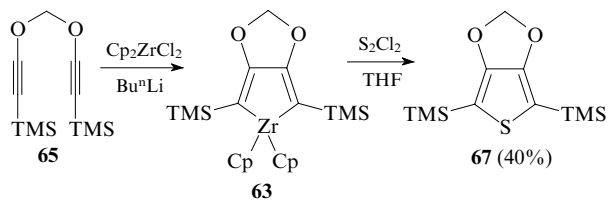
Scheme 38



R^1 = CH_2OMe, R^2 = TMS;

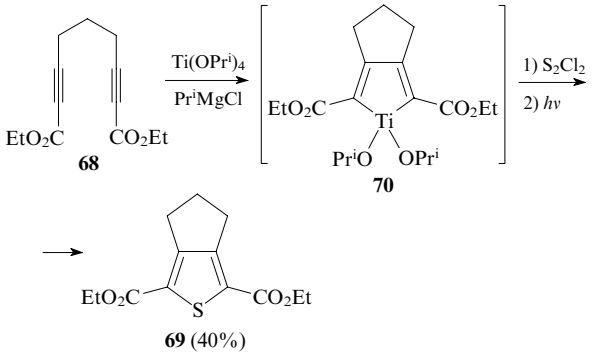
$R^1–R^1$ = n-C_8H_{17}––C_8H_{17}-n, R^2 = Th;

TMS is trimethylsilane, Th is thienyl



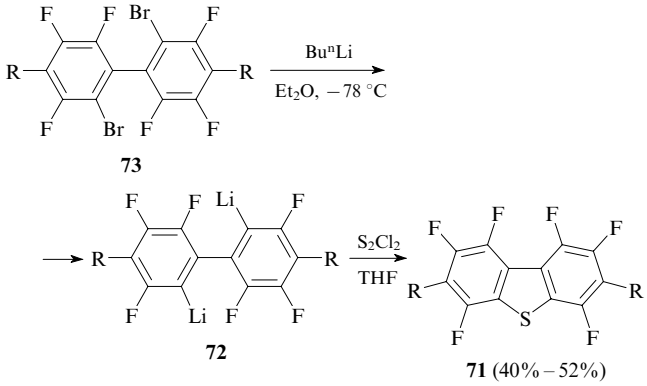
Diethyl 2,7-nonadiynedioate **68** is converted into thiophene **69** through the stage of formation of titanacyclopentadiene **70** with the use of titanium tetraisopropoxide and isopropylmagnesium chloride.[65] As distinct from the reactions of zirconocenes, the reaction of diyne **68** with sulfur monochloride leading to thiophene requires UV irradiation (< 300 nm), presumably, for elimination of the excessive sulfur atom (Scheme 39).[66]

Scheme 39



Fused thiophenes **71** with polyfluorinated benzene rings form in the reaction of S_2Cl_2 with dilithium derivatives **72**,[67] synthesized from dibromo derivatives **73** (Scheme 40).

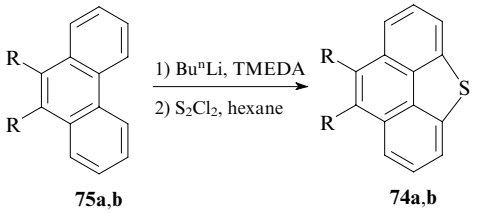
Scheme 40



R = F, C≡CPh

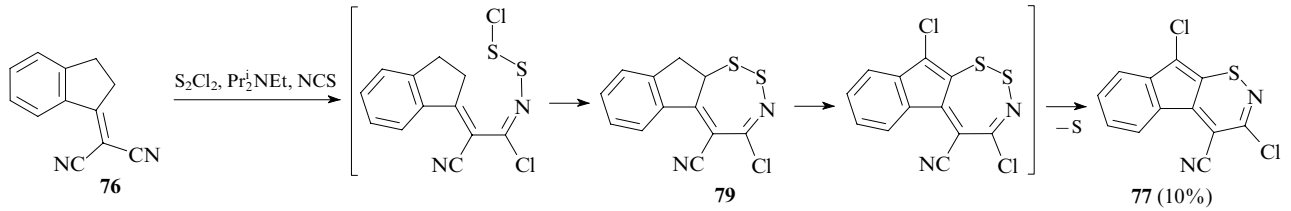
Phenanthro[4,5-*b*,*c*,*d*]thiophene (**74a**) and triphenyleno[1,12-*b*,*c*,*d*]thiophene (**74b**) are also synthesized through the stage of formation of lithium derivatives generated *in situ* from polycyclic compounds — phenanthrene (**75a**) and triphenylene (**75b**) (Scheme 41).[68] The yields of the products are comparable with the yields achieved in the reactions of dibromo aromatic compounds.

Scheme 41



R = H (**a**, yield 34%), R–R is benzo (**b**, 44%); TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine

Scheme 42

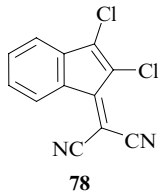


NCS is chlorosuccinimide

b. 1,2- and 1,4-Thiazines

The reaction of dicyanomethylideneindane (**76**) with sulfur monochloride, diisopropylethylamine and *N*-chlorosuccinimide in tetrahydrofuran at 0 °C for 3 days affords fused 1,2-thiazine **77** in low yield (Scheme 42). The major product of this transformation is dichloro derivative **78** (70%).[69]

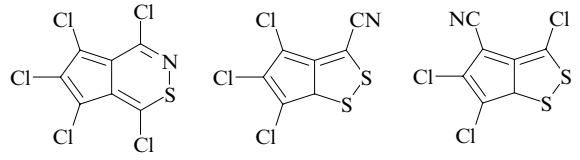
Structure 78



The most likely mechanism of conversion of dicyanide **76** into thiazine **77** involves the addition of S_2Cl_2 to the nitrile group with subsequent cyclization at the activated C–H position into diazepine **79**; the latter, after chlorination–dehydrochlorination and sulfur atom extrusion, forms planar and formally aromatic product **77** (see Scheme 42).

Bicyclo[3.2.0]hept-2-en-6-one oxime (**80**) reacts with the same system of reagents to give cyclopenta-1,2-thiazine **81** and two other unexpected 10π-electron pseudoazulenes **82** and **83** (all of them in low yields).[70]

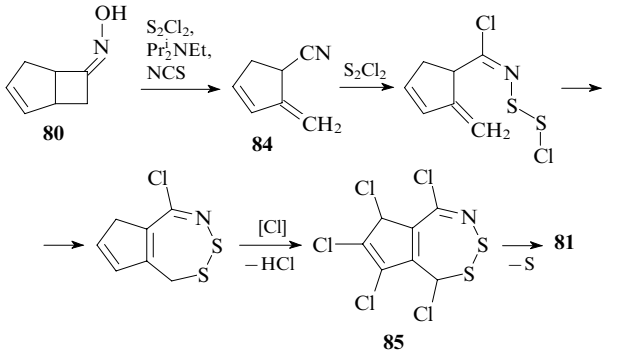
Structures 81–83



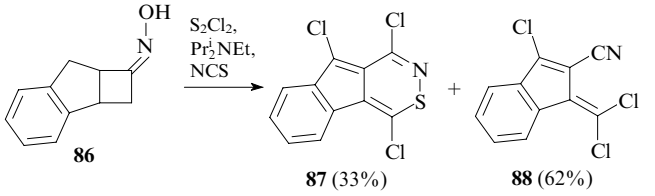
The simplest mechanism of transformation of oxime **80** to 1,2-thiazine **81** can involve a second-order Beckmann rearrangement initiated by sulfur monochloride. The cyclobutane ring is opened to form nitrile **84**. The latter adds to S_2Cl_2 and forms a seven-membered diazepine derivative. Then, common chlorination–dehydrochlorination processes lead to perchlorinated product **85** (Scheme 43). The latter is formally a 12π-electron system and can undergo contraction of the seven-membered ring to a fused [6 + 3] cyclic system with a loss of the sulfur atom.

A benzo derivative of oxime **80** — compound **86** — forms, under similar conditions, side product **87** close in structure to thiazine, and perchlorinated methylideneindene **88** is isolated as the major product (Scheme 44).

Scheme 43

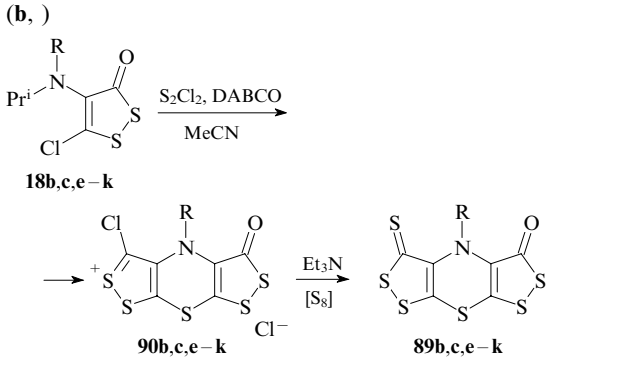


Scheme 44



Study of reactions of 5-chloro-1,2-dithiol-3-ones **18b**,**c**,**e**–**k** with sulfur monochloride in the presence of DABCO has shown that they occur only in acetonitrile, a solvent rather rarely used in processes involving S_2Cl_2. Treatment of the reaction mixture with triethylamine leads to formation of tricyclic bis(dithiolo)thiazines **89b**,**c**,**e**–**k** in yields varying from moderate to high.[71] The authors assume that, in this case, there is successive formation of 1,2-dithiole and 1,4-thiazine rings (Scheme 45).

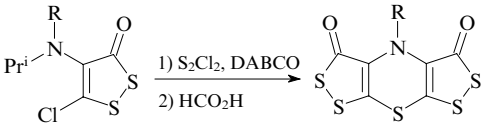
Scheme 45



R = $(CH_2)_2Cl$ (**b**, yield 40%), $(CH_2)_2Phth$ (**c**, 68%), $(CH_2)_2N_3$ (**e**, 65%), $(CH_2)_2CO_2Et$ (**f**, 73%), $(CH_2)_2SPh$ (**g**, 54%), $(CH_2)_2CN$ (**h**, 49%), $(CH_2)_2SO_2Ph$ (**i**, 44%), $(CH_2)_2OC(O)H$(**j**, 78%), Bn (**k**, 62%)

It is evident that key intermediate reaction products are 3-chlorodithiolium salts **90b**,**c**,**e**–**k**. They react with a sulfur-containing nucleophile (formed from a base and elemental sulfur) to give the thione group.[72] The use of an oxygen-containing nucleophile (most frequently, formic acid is used) at the final stage instead of triethylamine leads to diketones **91b**,**c**,**e**–**h**,**k** in moderate to high yields (Scheme 46).

Scheme 46

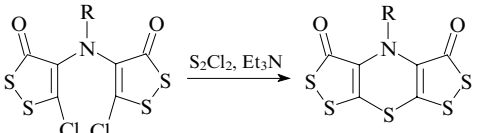


18b,**c**,**e**–**h**,**k** **91b**,**c**,**e**–**h**,**k**

R = $(CH_2)_2Cl$ (**b**, yield 78%), $(CH_2)_2Phth$ (**c**, 54%), $(CH_2)_2N_3$ (**e**, 58%), $(CH_2)_2CO_2Et$ (**f**, 65%), $(CH_2)_2SPh$ (**g**, 56%), $(CH_2)_2CN$ (**h**, 49%), Bn (**k**, 41%)

In an attempt to extend the sulfurating ability of sulfur monochloride to other objects, the reaction has been carried out with *N*,*N*-bis(5-chloro-3-oxo-1,2-dithiol-4-yl)amines **92a**,**c**,**f**–**h**,**k**. The reaction of these compounds with a mixture of S_2Cl_2 and triethylamine in chloroform affords bis(dithiolo)thiazines **91a**,**c**,**f**–**h**,**k** in high yields (Scheme 47).[71]

Scheme 47



92a,**c**,**f**–**h**,**k** **91a**,**c**,**f**–**h**,**k**

R = Et (**a**, yield 93%), $(CH_2)_2Phth$ (**c**, 95%), $(CH_2)_2CO_2Et$ (**f**, 82%), $(CH_2)_2SPh$ (**g**, 87%), $(CH_2)_2CN$ (**h**, 80%), Bn (**k**, 79%)

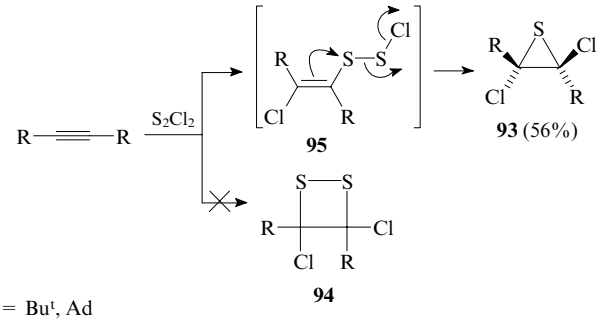
In this case, the 1,4-thiazine ring is a result of unusual substitution of a sulfur atom for the chlorine atoms in the reaction with electrophilic sulfur monochloride and its mixtures with tertiary amines.

c. Other heterocycles

Three-, five-, six- and seven-membered heterocyclic compounds can be obtained from different organic substrates and sulfur monochloride.

The reaction of di-*tert*-butyl- and bis(1-adamantyl)acetylenes with S_2Cl_2 unexpectedly leads to dichlorothiiranes **93** in high yield.[73] At the same time, expected dithietanes **94**

Scheme 48



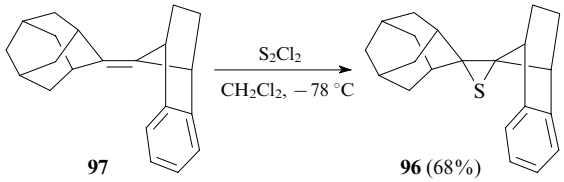
95 **93** (56%) **94**

R = Bu^t, Ad

are not formed even in trace amounts. The authors suggest that the first stage of the reaction is the addition of sulfur monochloride to the triple bond to form adducts **95** in a configuration favourable for avoiding steric interaction between bulky substituents. Then, sulfur elimination leads exclusively to thiiranes **93** (Scheme 48).

Bis-spiro-substituted *syn*-thiirane **96** forms in 68% yield when 2-adamantylidene-9-benzonorbornenylidene (**97**) is treated with sulfur monochloride at low temperature.[74] It is worth noting that sulfur dichloride reacts with alkene **97** to give thiirane **96** in higher yield than the reaction with S_2Cl_2, which is a rather rare exception (Scheme 49).

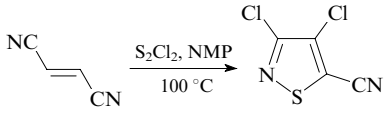
Scheme 49



97 **96** (68%)

With the use of sulfur monochloride, different five-membered heterocycles containing two or three heteroatoms have been synthesized. In particular, an efficient method of synthesis of 3,4-dichloro-5-cyanoisothiazole (**98**) from commercially available fumaronitrile and sulfur monochloride in *N*-methyl-2-pyrrolidone (NMP) at 100 °C was developed by Japanese researchers (Scheme 50).[75]

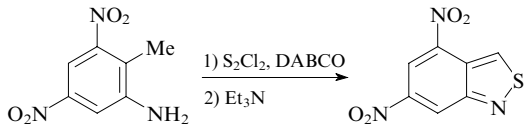
Scheme 50



98 (92%)

The reaction of 2-methyl-3,5-dinitroaniline with sulfur monochloride in the presence of DABCO in chloroform followed by addition of triethylamine leads to fused 4,6-dinitrobenzo[*c*]isothiazole (**99**) in high yield (Scheme 51).[76] Previously, only one example of formation of the isothiazole ring from vicinal amino and methyl groups with participation of sulfur monochloride has been described.[77]

Scheme 51

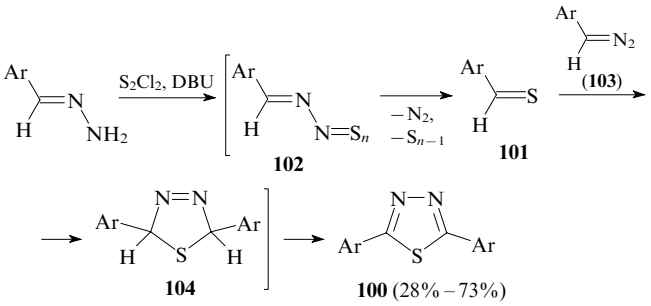


99 (90%)

Hydrazones are suitable initial compounds for synthesis of 1,3,4-thiadiazoles. Benzaldehyde hydrazone and its derivatives react with sulfur monochloride in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to form 2,5-diaryl-1,3,4-thiadiazoles **100** in moderate to high yields.[78] The authours believe that the formation of the thiadiazole ring is a result of interaction of two different molecules formed from hydrazone and S_2Cl_2 — thioaldehyde **101** (the product of nucleophilic attack of the hydrazone at S_2Cl_2 with subsequent elimination of the nitrogen molecule from

unstable *N*-thionitrosoimine **102**) and diazoalkane **103** (the product of oxidation of the initial hydrazone with the same sulfur monochloride). 1,3-Dipolar cycloaddition of these molecules leads to 1,3,4-thiadiazoline **104**, which is further oxidized to the target product, thiadiazole **100** (Scheme 52).

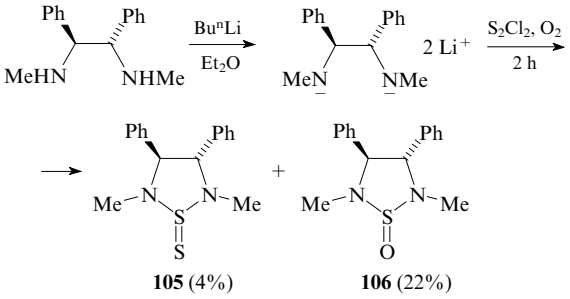
Scheme 52



Ar = 4-XC_6H_4 (X = H, OMe, F, Cl, Br, CF_3); *n* = 1 or 2

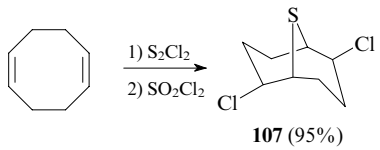
Uncommon and rare thiosulfinyl derivative of 1,2,5-thiazolidine **105** has been obtained by the reaction of dilithium salt of *N*,*N*′-dimethyl-1,2-diphenylethylenediamine with sulfur monochloride.[79] The yield of **105** is very low since the reaction is accompanied by its oxidation or hydrolysis to *S*-oxide **106**. In addition, some fraction of the initial amine remains unreacted (Scheme 53).

Scheme 53



The treatment of 1,5-cyclooctadiene first with sulfur monochloride and then with sulfuryl chloride leads to a high yield of 2,6-dichloro-9-thiabicyclo[3.3.1]nonane **107**, containing two six-membered tetrahydrothiopyrane rings (Scheme 54).[80]

Scheme 54

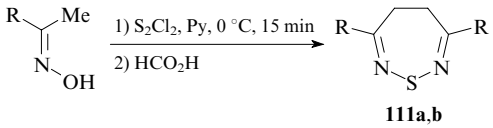


The formation of thiopyrane **107** is explained by the authors as a result of the reversible addition reaction of SCl_2, which is in equilibrium with sulfur monochloride. In addition, this bicycle is thermodynamically highly stable as compared with the other possible products of sulfur dichloride addition.

Resonance-stabilized bis(thiadiazino)pyridine **108** has been synthesized from bifunctional amidine **109** and sulfur monochloride with subsequent treatment of intermediate salt **110** with $NOSbF_6$ and proton sponge (Scheme 55).[81,82]

Seven-membered dihydro-1,2,7-thiadiazepine **111a** is a result of the unexpected dimerization of 4-nitro-substituted acetophenone oxime under the action of sulfur monochloride.[83] Analogous product **111b** has been synthesized by the reaction of 2-acetylbenzofuran oxime under the same conditions (Scheme 56).[84]

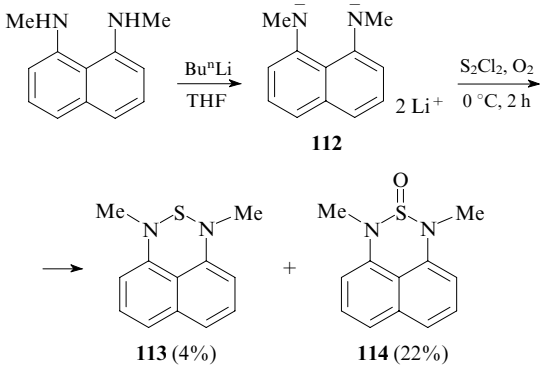
Scheme 56



R = 4-$O_2NC_6H_4$ (**a**, yield 33%), 2-benzofuryl (**b**, 25%)

The reaction of dilithium salt of 1,8-bis(methylamino)-naphthalene (**112**) with S_2Cl_2 in tetrahydrofuran leads to fused dihydrothiadiazine **113**, which is unstable in air and is oxidized to the corresponding *S*-oxide **114** in the course of isolation (Scheme 57).[79]

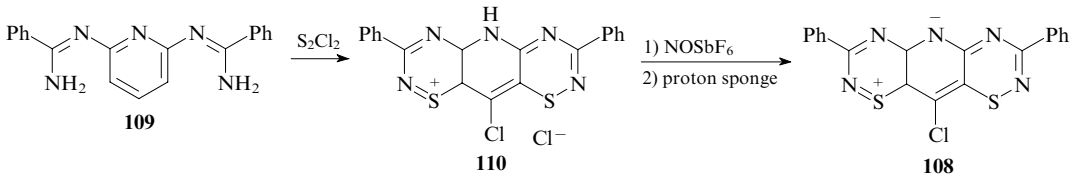
Scheme 57



2. Heterocycles with two introduced sulfur atoms

Heterocycles with two bonded sulfur atoms, for example, 1,2-dithioles or 1,2,3-dithiazoles, are the most expected products of reactions with sulfur monochloride, since they can form upon direct insertion of the S_2 fragment into the molecule. However, even in these cases, the basic process can be accompanied by unexpected transformations, including, *e.g.*, the formation of another heterocycle.

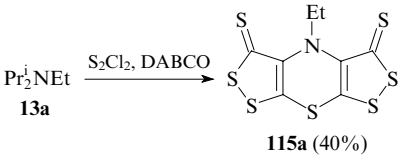
Scheme 55



a. 1,2-Dithioles

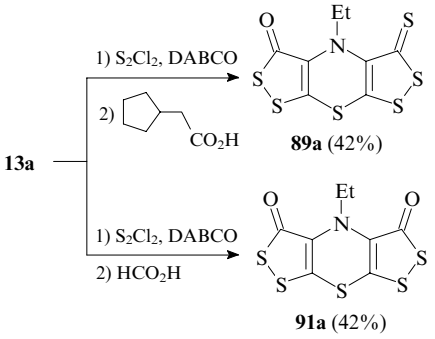
Synthesis from isopropylamines. The strategy of synthesis of 1,2-dithioles from tertiary isopropylamines and sulfur monochloride was proposed and developed by the authors of this review in collaboration with Prof. Rees from Imperial College London in the late 1990s and early 2000s. It has been revealed[85] that diisopropylethylamine (**13a**), which was used in reaction with sulfur monochloride as an inert base, is able quite unexpectedly to react with S_2Cl_2 and 1,4-diazabicyclooctane to form a new polysulfur-containing heterocyclic system — bis(1,2-dithiolo)-1,4-thiazine (**115a**). In this one-pot transformation, 14 isopropyl C–H bonds of Hunig's base are replaced by ten C–S bonds and two C=C bonds, whereas the ethyl group remains intact (Scheme 58).

Scheme 58



Other bis(dithiolo)(dithiolo)thiazine (**89a** and **91a**) have also been synthesized by the reactions of Hunig's base with sulfur monochloride with addition at the final stage of oxygen donors, such as cyclopentylacetic and formic acids (Scheme 59).[72]

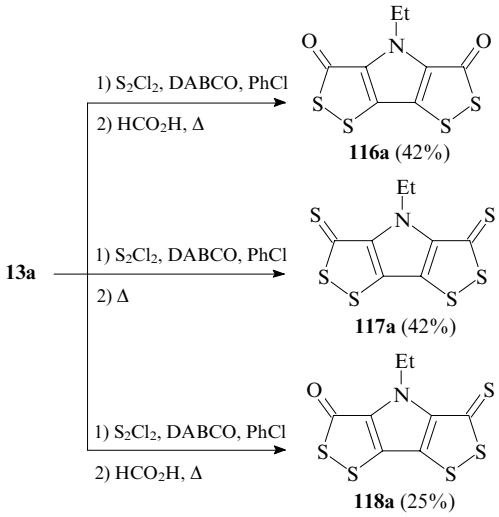
Scheme 59



The reaction in a high-boiling solvent, for example, chlorobenzene, leads to bis(1,2-dithiolo)pyrroles **116a**, **117a** and **118a** through elimination of a sulfur atom from intermediate bis(dithiolo)thiazines **91a**, **115a** and **89a**, respectively (Scheme 60).[86]

The transformation of Hunig's base to bis(dithiolo)thiazines and then to pyrroles requires 15 (or even more) separate stages. The most probable mechanism of this

Scheme 60

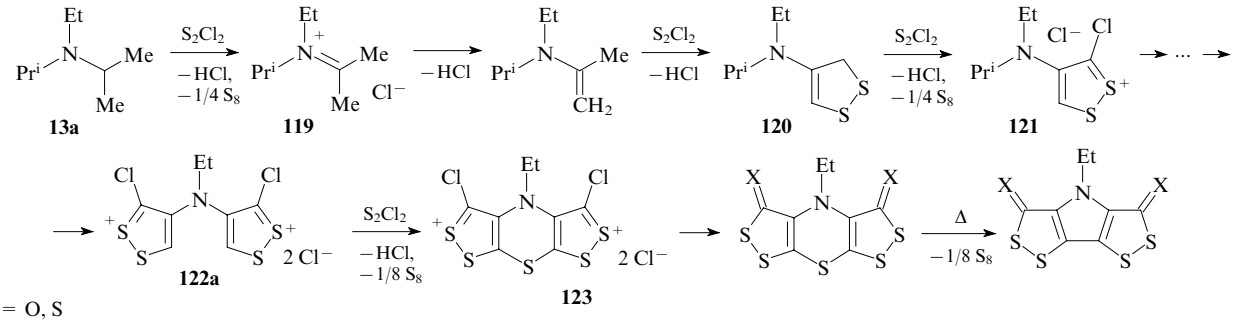


reaction is presented in Scheme 61.[72] Initially, one of the isopropyl groups of Hunig's base can be oxidized to generate iminium cation **119**, as is commonly suggested for the oxidation of tertiary amines.[87] Deprotonation of cation **119** leads to the corresponding enamine, which reacts with S_2Cl_2 to give successively 1,2-dithiole **120** and 3-chlorodithiolium salt **121**. The dithiolium ring is rather stable, and such a sequence of transformations can be repeated with participation of the second isopropyl group to give dication salt **122a**. The latter is cyclized under the action of sulfur monochloride to form the 1,4-thiazine ring in compound **123**. Dication salt **123** is a key intermediate in all these transformations. Then, this salt reacts with sulfur- and oxygen-containing nucleophiles to give either bis(dithiolo)-thiazines or bis(dithiolo)pyrroles, depending on the reaction conditions.

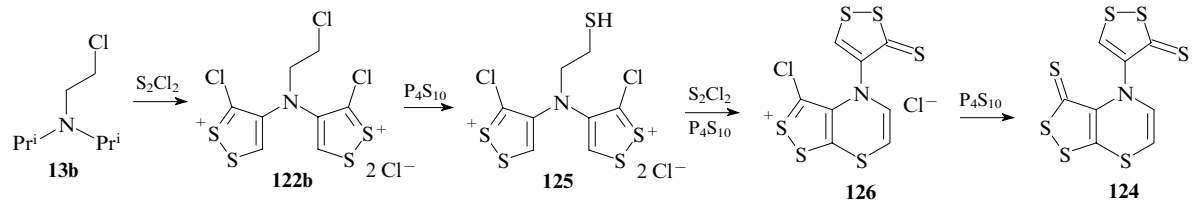
Applying these conditions to other substituted diisopropylamines, the authors synthesized a number of bis(dithiolo)thiazines, including those unsubstituted at the nitrogen atom.[88, 89]

Treatment of diisopropyl(2-chloroethyl)amine (**13b**) with sulfur monochloride followed by addition of P_4S_{10} leads to dithiolothiazine **124**.[90] The formation of this product can be explained in the following way: salt **122b** (analogous in structure to salt **122a**) in the presence of P_4S_{10} is converted into salt **125**, which is cyclized to form a thiazine ring. Sulfuration of salt **126** to thiazine **124** evidently occurs under the action of the same reagent — P_4S_{10} (Scheme 62).

Scheme 61

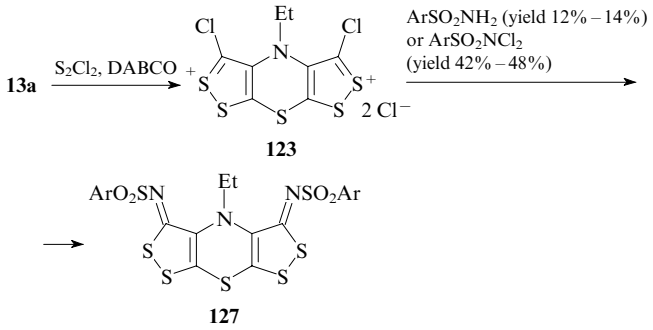


Scheme 62



3,5-Dichlorodithiolium salt **123**, obtained from diisopropylethylamine, S_2Cl_2 and DABCO in chloroform at room temperature, reacts with arylsulfamides and their *N,N′*-dichloro derivatives to form diimines — bis(arylsulfonylimino)bis(dithiolo)thiazines **127** — in moderate yield (Scheme 63).[91]

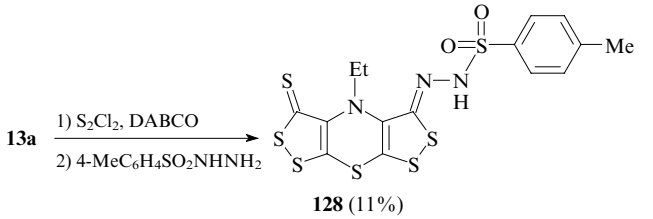
Scheme 63



Ar = Ph, 4-MeC_6H_4

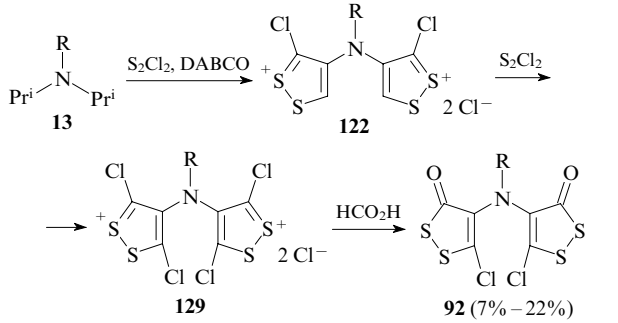
The reaction of Hunig's base, sulfur monochloride and *p*-toluenesulfonyl hydrazide under similar conditions follows a more complicated pathway and leads to monohydrazide **128** in low yield (Scheme 64).[91]

Scheme 64



The reaction of n-alkyldiisopropylamines with sulfur monochloride and a deficient amount of DABCO (with respect to S_2Cl_2) does not lead to closure of the 1,4-thiazine ring, so that it stops at the stage of formation of salt **122**. The latter is chlorinated by an excess of S_2Cl_2 to salts **129** and, after treatment with formic acid, gives *N,N*-bis(5-chloro-3-oxo-1,2-dithiol-4-yl)amines **92** in low yield.[92] The corresponding bis(dithiolo)thiazines **91** are isolated as by-products (Scheme 65).

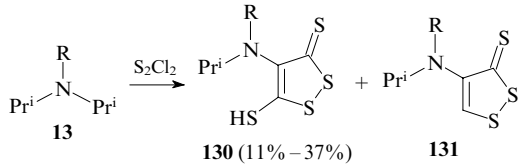
Scheme 65



R = Et, Bn, $(CH_2)_2Cl$, $(CH_2)_2SPh$, *etc.*

In all transformations described in this section, both isopropyl groups in *N*-alkyldiisopropylamines are converted into 1,2-dithiole rings. It has been demonstrated[93] that the reaction can be stopped after the formation of monocyclic 1,2-dithioles, and the crucial factor for successful synthesis of monodithioles is low temperature of the reaction. The reaction of *N*-alkyldiisopropylamines and S_2Cl_2 in chloroform in the absence of another base at 0 °C yields monocyclic 1,2-dithiole-3-thiones **130** and **131**; in all reactions, the major products are 5-sulfanyl derivatives **130** (Scheme 66).

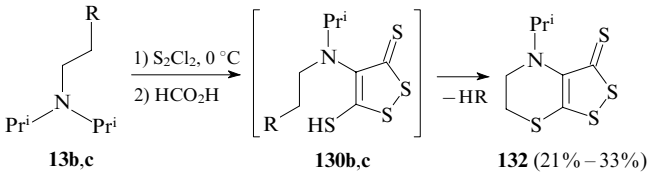
Scheme 66



R = Et, Bn, $(CH_2)_2CO_2Et$, $(CH_2)_2CN$, $(CH_2)_2N_3$, *etc.*

Interesting results have been obtained for the reaction of substituted diisopropylamines **13b**,**c** with S_2Cl_2. Instead of the expected sulfanyldithiolethiones, dithiolothiazine **132** has been isolated. It is suggested that the reaction leads to intermediate thiones **130b**,**c**; the latter undergo elimination of, respectively, HCl or phthalimide to give bicyclic structure **132** (Scheme 67).[94]

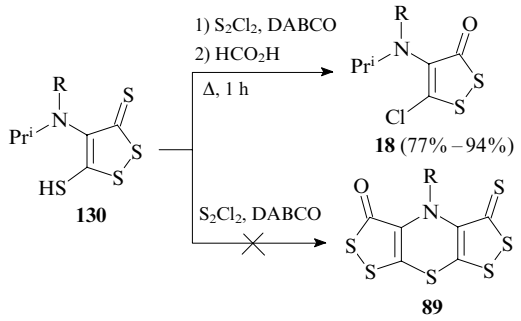
Scheme 67



R = Cl (**b**), Phth (**c**)

The synthesized sulfanyldithiolethiones **130** have been introduced into the reaction with a mixture of S_2Cl_2 and DABCO under the conditions of formation of tricyclic bis(dithiolo)thiazine **89** from substituted diisopropylamines.[72] However, against expectations, the reaction in all cases leads to 5-chlorodithiol-3-ones **18** in high yields [except compound **18a** (R = Et), which is not formed under given conditions] (Scheme 68).[94]

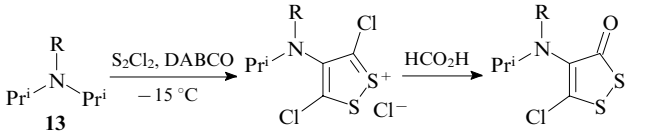
Scheme 68



R = Bn, $(CH_2)_2CO_2Et$, $(CH_2)_2CN$, $(CH_2)_2N_3$

It has been demonstrated later that 5-chloro-1,2-dithiol-3-ones **18** can be obtained directly from *N*-alkyldiisopropylamines, S_2Cl_2 and DABCO in moderate to high yields when the reaction is carried out at low temperature (−15 °C) and the reaction mixture is then treated with formic acid (Scheme 69).[71]

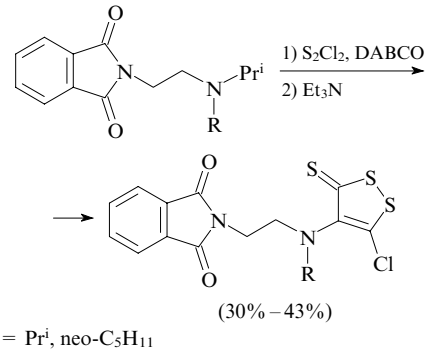
Scheme 69



R = Bn, $(CH_2)_2Phth$, $(CH_2)_2Cl$, $(CH_2)_2N_3$, $(CH_2)_2CO_2Et$, $(CH_2)_2SPh$, $(CH_2)_2CN$, $(CH_2)_2SO_2Ph$, $(CH_2)_2OC(O)H$

Structurally similar 5-chloro-1,2-dithiole-3-thiones have been synthesized by the reaction of alkylisopropyl(2-phthalimidoethyl)amines with a mixture of sulfur monochloride and DABCO and subsequent treatment with triethylamine (Scheme 70).[95] The unexpected stability of such thiones has been attributed to dipole–dipole interaction between the electron-releasing 1,2-dithiole-3-thione ring and the electron-withdrawing phthalimide group.

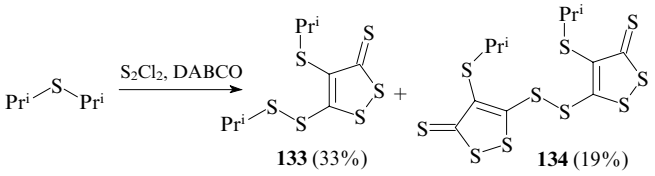
Scheme 70



R = Pr^i, neo-C_5H_{11}

The reaction of diisopropyl sulfide with sulfur monochloride and DABCO yields 1,2-dithiole-3-thiones **133** and **134** (Scheme 71).[96] It is believed that the formation of the dithiole ring occurs by a mechanism analogous to the mechanism of its formation from diisopropylamines. However, in the case of diisopropyl sulfide, only one isopropyl group reacts, while the second group is presumably deactivated upon the introduction of the dithiolethione fragment at the sulfur atom.

Scheme 71

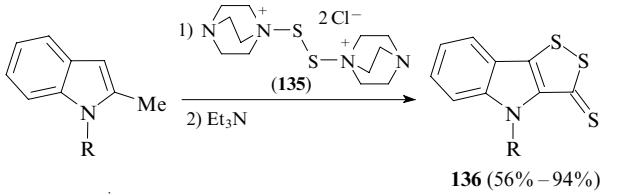


Synthesis from other substrates. The general strategy of synthesis of 1,2-dithioles in the other literature sources consists in the addition of two sulfur atoms to the CH═CH−CH moiety, and the methine groups should be activated. Earlier, elemental sulfur was commonly used for such transformations; however, recently, this reagent has been successfully replaced by sulfur monochloride.

In the previous section, it has been shown that *N*-isopropyl groups can be converted into *N*-(1,2-dithiole-3-thione) moieties. Nitrogen-containing heterocycles with CH_3 and CH groups in the *ortho*-position, for example, readily available 2-methylindoles, are structurally similar to the *N*-isopropyl group and can be used as initial compounds in synthesis of dithioloindoles.

The treatment of *N*-alkyl- and *N*-benzyl-2-methylindoles with a fivefold excess of salt **135**, obtained from sulfur monochloride (1 equiv.) and DABCO (2 equiv.), in chloroform at room temperature with subsequent addition of triethylamine leads to fused dithioloindoles **136** in moderate to high yields (Scheme 72).[13]

Scheme 72

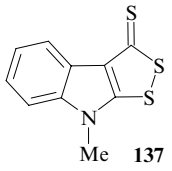


R = Me, Et, Pr^i, Bn

N-Acetyl- and *N*-benzoyl-2-methylindoles do not react with S_2Cl_2 and DABCO even under more severe conditions; only the initial indoles have been isolated in high yield from the reaction mixture. It is evident that electron-withdrawing substituents at the nitrogen atom of the indole ring (acetyl and benzoyl groups) suppress the reaction with electrophilic sulfur monochloride.

It is worth noting that the isomer of indolodithiole **136** — 8-methyl-1,2-dithiolo[3,4-*b*]indole-3(8*H*)-thione **137** — is not formed in the reaction of 1,3-dimethylindole (**10**) with S_2Cl_2 in the presence of DABCO. In this case, sulfur monochloride chlorinates both the pyrrole and benzene rings (see Section II.1.a).[13]

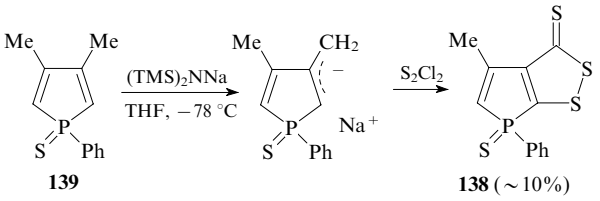
Structure 137



It is interesting that, almost at the same time with this study, Ciric and Mathey[97] described the synthesis of 1,2-dithiole-3-thione annelated with the phosphole ring **138**. It has been synthesized from corresponding heterocycle **139**,

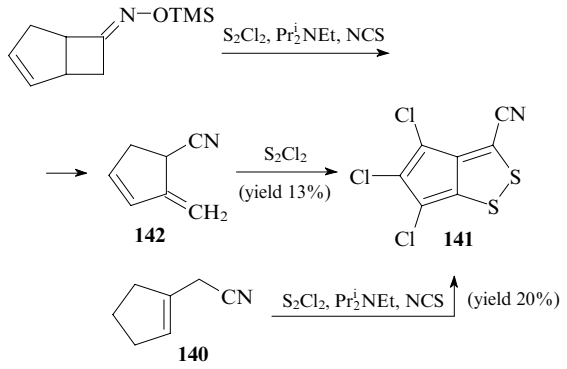
in which the methyl and C–H groups are *ortho* to each other. In this case, for the reaction with S_2Cl_2 to occur, activation with a base (for example, with sodium hexamethyldisilazide) is necessary. However, the yield of fused dithiolethione **138** is only 10% (Scheme 73).

Scheme 73



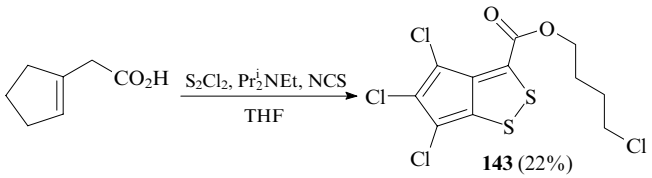
1-(Cyanomethyl)cyclopentene **140** reacts with sulfur monochloride, Hunig's base (**13a**) and *N*-chlorosuccinimide to form perchlorinated cyclopenta-1,2-dithiole **141**.[98] The same product has been synthesized from the trimethylsilyl derivative of *cis*-bicyclo[3.2.0]hept-2-en-6-one oxime. In this case, its formation is explained by the second-order Beckmann rearrangement to cyanide **142** with subsequent cyclization, exhaustive chlorination and dehydrochlorination (Scheme 74).

Scheme 74



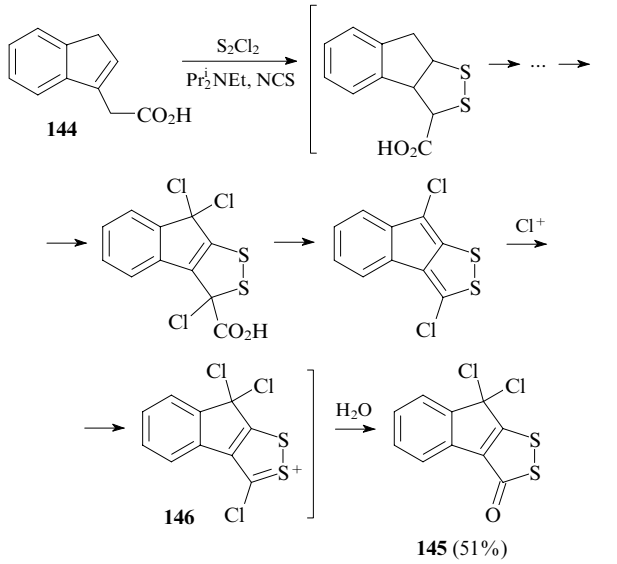
Cyclopentenylacetic acid reacts with a mixture of sulfur monochloride, Hunig's base and *N*-chlorosuccinimide in tetrahydrofuran to form trichlorocyclopenta-1,2-dithiole-3-carboxylate **143**. This product is a result of a series of transformations — heterocyclization, chlorination–dehydrochlorination and unexpected esterification of the acid in tetrahydrofuran to its 4-chlorobutyl ester **143** (Scheme 75).[99]

Scheme 75



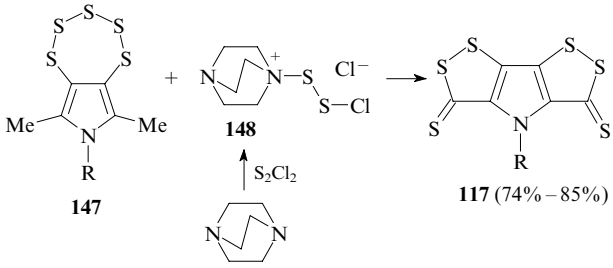
Under the same conditions, indenylacetic acid **144** gives four different products; the major product among them is 1,2-dithiolone **145**.[69] Although a similar transformation of indenylacetic acid was hard to predict, the corresponding mechanism can be easily described on the basis of the previously discovered properties of the sulfur monochloride–Hunig's base (**13a**)–*N*-chlorosuccinimide system. Such a system is able to cyclize activated allyl structures with subsequent exhaustive chlorination–dehydrochlorination, which leads to completely unsaturated and chlorinated products. It is suggested that intermediate 1,2-dithiolecarboxylic acid can be decarboxylated to form 3-chloro-1,2-dithiolium salt **146**, which reacts with an oxygen source (for example, water traces) to give ketone **145** (Scheme 76).

Scheme 76



Pentathiepinopyrroles **147** react with salt **148**, synthesized from sulfur monochloride (1 equiv.) and DABCO (1 equiv.), to form bis(1,2-dithiolo)pyrroles **117** in high yield (Scheme 77).[100] Pentathiepins usually do not react with the S_2Cl_2–DABCO system at room temperature; therefore, it has been suggested that salt **148** reacts with its methyl groups as an electrophilic reagent to give bis(1,2-dithiolo)pyrroles **117** in the course of a complicated cascade of transformations.

Scheme 77



R = Me, Et, Pr^n, Pr^i, Bn

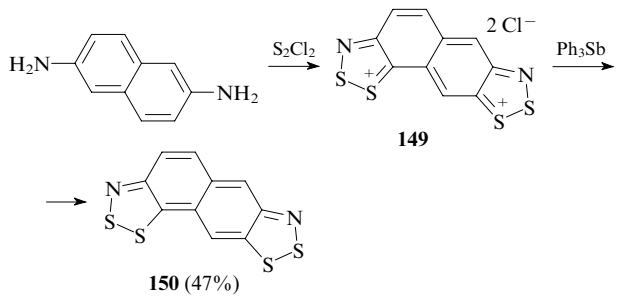
b. 1,2,3-Dithiazoles

Synthesis from amines. Synthesis of salts of 1,2,3-dithiazoles fused with benzene or heteroaromatic rings (so-called Herz salts) from sulfur monochloride and aromatic or heteroaromatic amines has been known for more than 90 years and is rather widely used by synthetic chemists. In this section, we consider modern examples of such syntheses.

Bis(1,2,3-dithiazoles) represent a new significant class of heterocycles for generation of free radicals. Considerable progress in this field is so-called 'double Herz condensation'. One of its examples is the reaction of 2,6-diaminonaphthalene with sulfur monochloride to give Herz salt **149**,

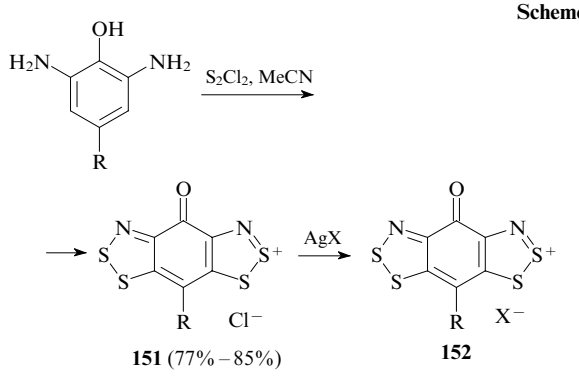
which is reduced with triphenylantimony to form a new tetracyclic system — naphthobis(1,2,3-dithiazole) **150** (Scheme 78).[101]

Scheme 78



Bis(1,2,3-dithiazolium) salts **151** have been obtained through the reaction of 2,6-diamino-4-chloro(phenyl)phenols with sulfur monochloride in acetonitrile.[102, 103] Chlorides **151** insoluble in organic solvents have been converted into soluble triflates or hexafluoroantimonates **152** by metathesis with corresponding silver salts (Scheme 79).

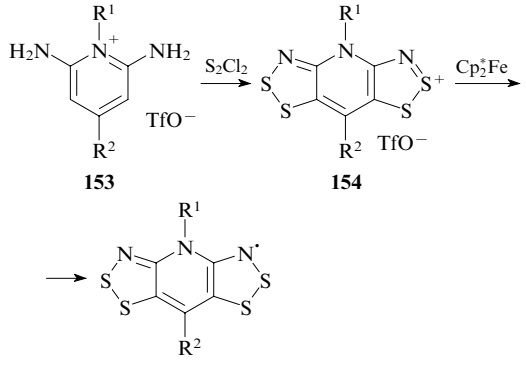
Scheme 79



R = Cl, Ph; X = TfO, SbF_6

The double Herz condensation of 2,6-diaminopyridinium salts **153** is an efficient method of synthesis of thiazolium salts **154**, which are readily reduced to corresponding radicals **155** through the reaction with decamethylferrocene.[104–107] It is interesting that 4-fluorinated pyridinium salts **153** (R^2 = F) are used for synthesis of fluorinated dithiazolyl radicals **155**.[108, 109] Although the same procedure is applied (heating under reflux with sulfur monochloride in acetonitrile for 1.5 h), the yields of salts **154** (R^2 = F) with substituents R^1 = Me and Et are rather different — 41% and 75%, respectively (Scheme 80).

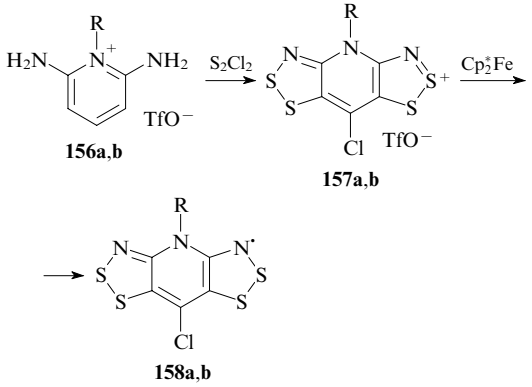
Scheme 80



R^1 = Me, Et; R^2 = Me, Ph, OMe, F;
Cp* is pentamethylcyclopentadienyl

If pyridinium salts with the unsubstituted 4-position **156a**,**b** are introduced into the reaction, the cyclization to 1,2,3-dithiazoles is accompanied by chlorination.[110, 111] Chlorinated salts **157a**,**b** are also easily converted into stable dithiazolyl radicals **158a**,**b** (Scheme 81).

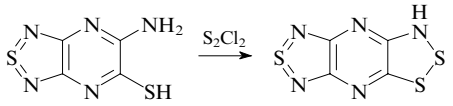
Scheme 81



R = Me (**a**, yield 83%), Et (**b**, 64%)

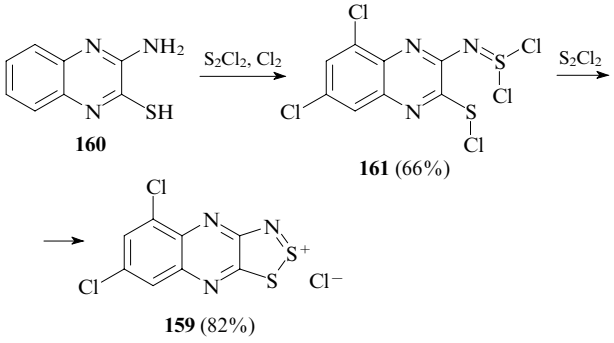
A series of fused 1,2,3-dithiazoles has been synthesized by Oakley and co-workers[112] by reactions of *o*-aminoaromatic thiols with sulfur monochloride. This approach is efficient, especially when Herz condensation cannot be accomplished (for some aromatic amines and phenylenediamines) (Scheme 82).

Scheme 82



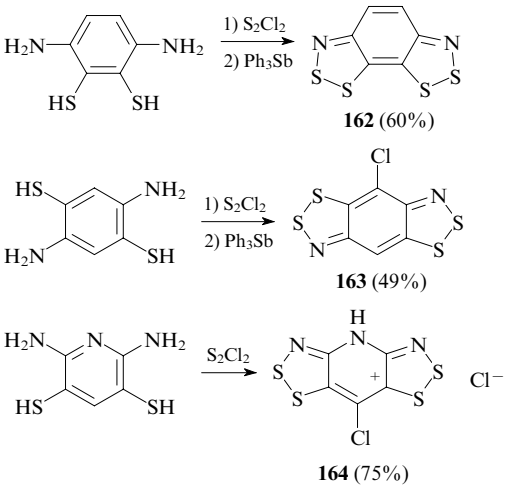
An uncommon strategy of two-stage synthesis of quinoxalino-1,2,3-dithiazolium chloride **159** has been proposed on the basis of the reaction of 3-amino-2-sulfanylquinoxaline (**160**) with a mixture of S_2Cl_2 and chlorine with subsequent treatment of intermediate compound **161** with sulfur monochloride[113] (Scheme 83).

Scheme 83



An important achievement of this method is synthesis of bis(1,2,3-dithiazoles) of aromatic and pyridine series from diaminodithioles.[114–116] In the case of aromatic derivatives, dithiazolium salts are usually not isolated; rather, they are reduced by triphenylantimony to neutral heterocyclic systems **162** and **163** (except salt **164**) (Scheme 84).

Scheme 84



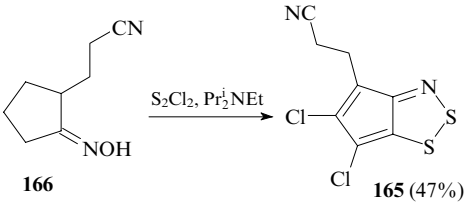
162 (60%)

164 (75%)

Synthesis from oximes. The reaction of formation of 1,2,3-dithiazoles and their salts from oximes and sulfur monochloride was discovered in the late 1970s and has been widely used until now.

In particular, cyclopenta-1,2,3-dithiazole **165** was obtained by the reaction of 2-substituted cyclopentanone oxime **166** with S_2Cl_2.[117] Like the formation of other cyclopentadithiazoles, this reaction is accompanied by exhaustive chlorination (Scheme 85).

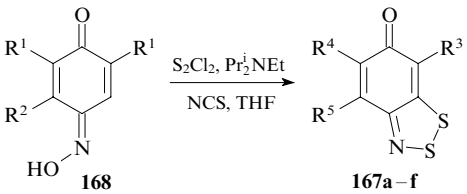
Scheme 85



166 **165** (47%)

1,2,3-Benzothiazol-6(6*H*)-ones **167** have been synthesized from *p*-benzoquinone oximes **168**, S_2Cl_2, diisopropylethylamine (**13a**) and NCS.[118] In some cases, the reaction is accompanied by chlorination of the benzoquinone moiety; substituents in the 2- and 6-positions of the ring are, as a rule, retained in target products, except *tert*-butyl groups, which are replaced by chlorine atoms (Scheme 86).

Scheme 86



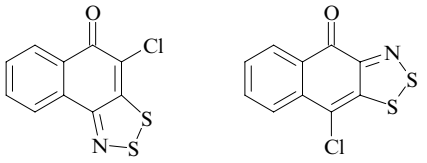
168 **167a–f**

R^1 = H, Cl, Me, Pr^i, Bu^t; R^2 = H, Me; R^3, R^4 = Cl, Me, Pr^i, CH_2Cl; R^5 = H, Cl, Me

Oximes of 1,4- and 1,2-naphthoquinones react analogously to form fused dithiazoles **169** and **170**.

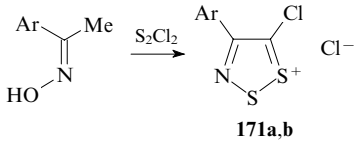
4-Aryl-5-chloro-1,2,3-dithiazolium salts **171a**,**b** were synthesized for the first time by the reaction of acetophenone oxime and its nitro derivative with sulfur monochloride in the mid-1990s by Rees and co-workers[83,119] (Scheme 87).

Structures 169, 170



169 **170**

Scheme 87

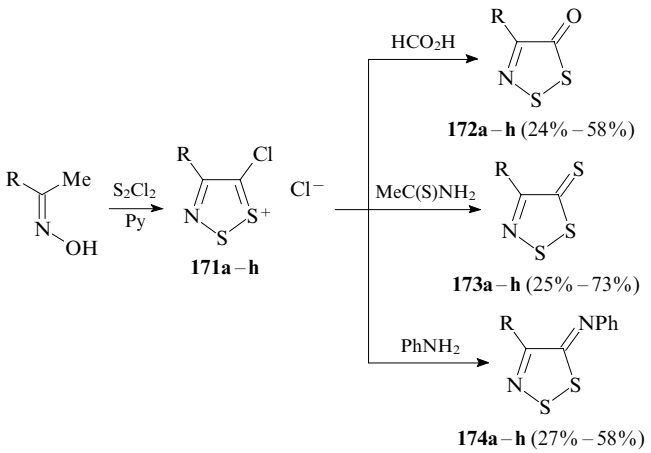


171a,**b**

Ar = Ph (**a**), 4-$O_2NC_6H_4$ (**b**)

Later, this approach has been intensively developed with participation of the authors of this review. It has been shown that the reaction can occur with readily available ethanone oximes of different structure containing aliphatic, aromatic and heteroaromatic substituents and functional groups.[120] Studies have shown that 1,2,3-dithiazolium salts **171** thus obtained are unstable; therefore, they are *in situ* introduced into further transformations. It has been demonstrated that 5-oxo- (**172**), 5-thioxo- (**173**) and 5-phenylimino-1,2,3-dithiazoles (**174**) are selectively formed in moderate to high yields by means of the one-pot reaction of ethanone oximes with sulfur monochloride and pyridine in acetonitrile followed by treatment with the corresponding nucleophile (formic acid, thioacetamide or aniline) (Scheme 88).

Scheme 88



172a–h (24%–58%)

171a–h

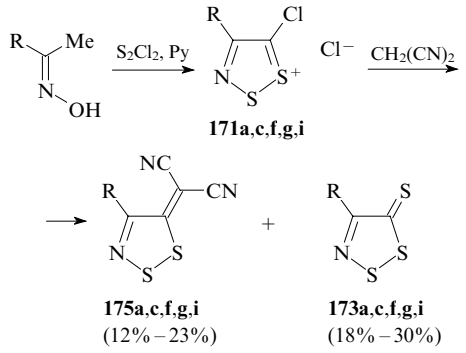
173a–h (25%–73%)

174a–h (27%–58%)

R = Ph (**a**), 4-$O_2NC_6H_4$ (**b**), 4-FC_6H_4 (**c**), 2-pyridyl (**d**), 2-benzofuryl (**e**), Th (**f**), Me (**g**), CO_2Et (**h**)

The salts of substituted 1,2,3-dithiazoles, prepared from ethanone oximes and sulfur monochloride, react with malononitrile less selectively.[121] In addition to the formation of 4-substituted 1,2,3-dithiazol-5(5*H*)-ylidenes **175**, the corresponding thiones **173** have been isolated from the reaction mixture. Both products have been obtained in low yields, which have not been improved despite numerous attempts of the authors (Scheme 89).

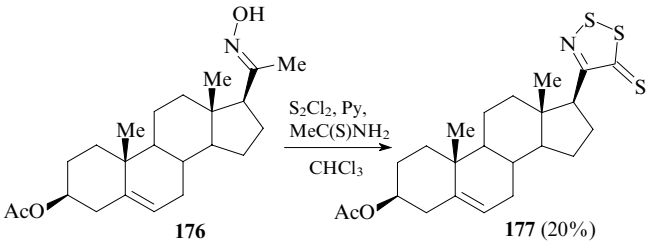
Scheme 89



R = Ph (**a**), 4-FC_6H_4 (**c**), Th (**f**), Me (**g**), 4-$MeOC_6H_4$ (**i**)

Synthesis of 1,2,3-dithiazole-5-thiones has also been extended to ethanone oxime containing a steroid moiety as a substituent.[122] In particular, the reaction of 3-acetoxy-5-pregnen-20-one oxime (**176**) with S_2Cl_2 and pyridine in chloroform (for better solubility of the steroid compound) followed by treatment with thioacetamide leads to thione **177** (Scheme 90).

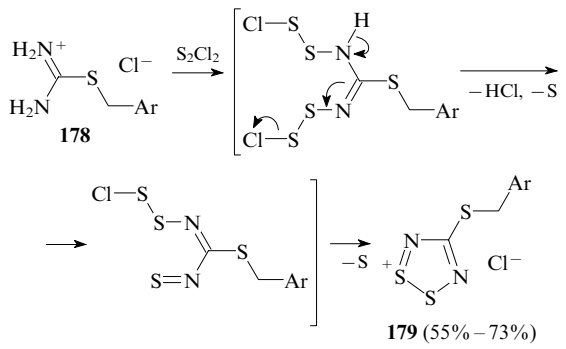
Scheme 90



c. Other heterocycles with two sulfur atoms

1,2,3,5-Dithiadiazolyl radicals have properties of organic molecular magnets and serve as the base of current-conducting materials; therefore, the methods of synthesis of their precursors — the corresponding 1,2,3,5-dithiadiazolium salts — have attracted much interest of researchers. The reaction of isothiuronium chlorides **178** with sulfur monochloride is a typical example of a suitable method of synthesis of 1,2,3,5-dithiadiazolium chlorides **179**.[123] On the basis of transformations of amidines and guanidines under the action of sulfur dichloride, leading to similar dithiadiazolium salts, the authors suggested the mechanism of formation of salts **179**. It involves the addition of two S_2Cl_2 molecules to amidine **178** and subsequent elimination of the HCl molecule and sulfur atom (Scheme 91).

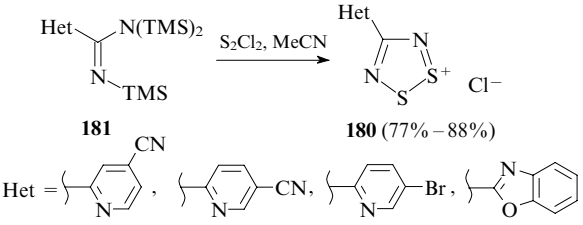
Scheme 91



Ar = Ph, 4-ClC_6H_4, 4-$F_3CC_6H_4$, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2,4-$(O_2N)_2C_6H_3$

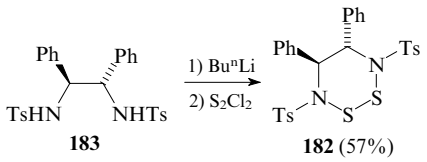
The synthesis of 1,2,3,5-dithiadiazolium salts **180** based on the reaction of tris(trimethylsilyl)amidine derivatives **181** with sulfur monochloride in acetonitrile.[124, 125] The yields of the salts containing heterocyclic substituents are, as a rule, high (Scheme 92).

Scheme 92



A previously undescribed six-membered heterocyclic system — 1,2,3,6-dithiadiazine **182** — has been synthesized from 1,2-diphenylethylenediamine **183** containing electron-accepting *p*-toluenesulfonyl (tosyl, Ts) groups at two nitrogen atoms. The reaction of the intermediate dilithium salt with sulfur monochloride has been carried out in diethyl ether (Scheme 93).[79]

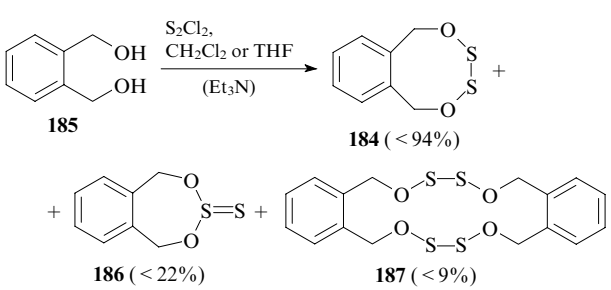
Scheme 93



It is interesting that the replacement of the tosyl groups in compound **183** by electron-releasing methyl groups changes the reaction pathway, and a five-membered ring is closed to form 2,5-dimethyl-3,4-diphenyl-1,2,5-thiadiazolidine 1-sulfide.

Synthesis of eight-membered cyclic dialkoxy disulfide **184** annelated to the benzene ring by the reaction of *o*-phenylenedimethanol (**185**) with sulfur monochloride opened the way to compounds of this class.[126] Detailed study of this reaction has shown that dialkoxy disulfide **184** in all cases is the major product; however, upon the introduction of triethylamine into the reaction mixture, other cyclic products — seven-membered thiosulfite **186** and 16-membered dimer **187** — can also form (Scheme 94).

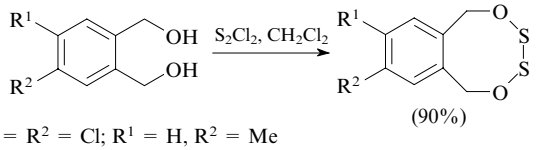
Scheme 94



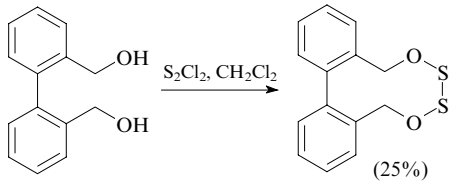
Analogous di(hydroxymethyl) derivatives also enter into this reaction to dioxadithia-containing heterocycles with a different number of atoms.[126, 127] The reaction at 5–10 °C

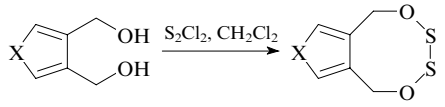
proceeds in 2–5 min, although the products are sometimes obtained in low yields (Scheme 95).

Scheme 95



$R^1 = R^2 = Cl$; $R^1 = H$, $R^2 = Me$

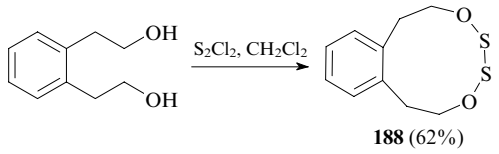




X = NPh (25%), O (88%)

It has been demonstrated that not only the dimethanol derivatives but also diethanol derivatives react in such a way. The reaction conditions remain the same, and the yield of dialkoxy disulfide **188** is 62% (Scheme 96).[127]

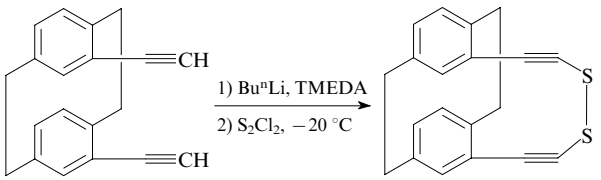
Scheme 96



188 (62%)

For bis(ethynyl)[2,2]paracyclophane **189** as an example, it has been shown that an S–S bridge can form between two triple bonds.[128] Disulfide **190** is synthesized under very mild conditions in moderate yield (Scheme 97).

Scheme 97

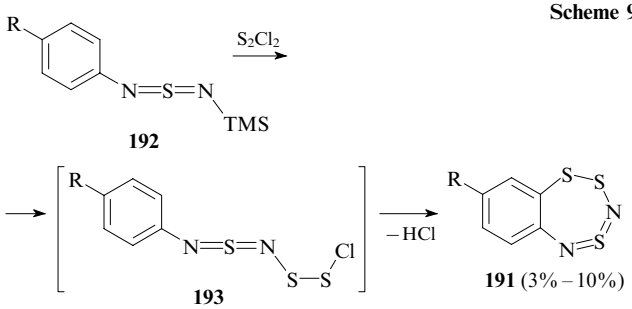


189 **190** (65%)

3. Heterocycles with three sulfur atoms

Asymmetric isomers of benzotrithiadiazepine **191** have been synthesized by condensation of azathienes **192** with sulfur monochloride and subsequent intramolecular *ortho*-cyclization of intermediate **193** (Scheme 98).[129]

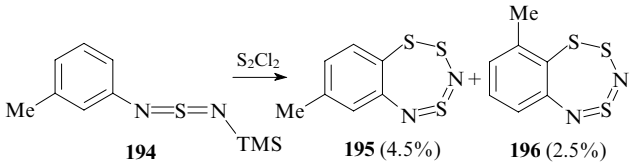
Scheme 98



R = H, Br

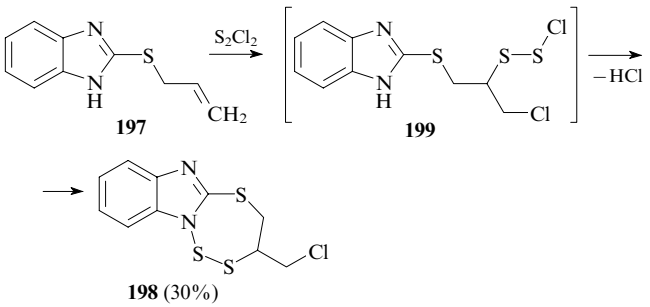
For *meta*-substituted azathiene **194**, an analogous reaction leads to a mixture of isomers with a higher content of 7-methyl derivative **195** as compared with 9-methyl isomer **196** (Scheme 99).

Scheme 99



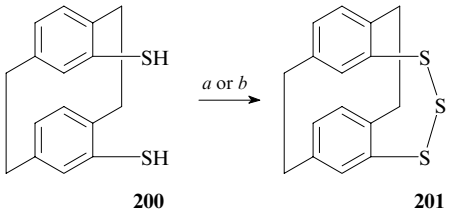
2-Allylthiobenzimidazole (**197**) reacts with sulfur monochloride to give trithiazepinobenzimidazole **198**.[35] It is suggested that the formation of this product occurs through elimination of the HCl molecule from intermediate compound **199**, which is obtained by the addition of S_2Cl_2 at the double bond of the allyl group (Scheme 100).

Scheme 100



The only product isolated from the reaction mixture containing dithioloparacyclophane **200** and sulfur monochloride turned out to be trisulfide **201** (yield 84%).[130] It is believed that this compound is obtained from the stage of formation of a polysulfur-containing heterocycle from which a sulfur atom is eliminated, which has been proved by isolation of elemental sulfur from the reaction mass. The reaction of dithiole **200** with sulfur dichloride leads to the same trisulfide **201** in higher yield (96%) (Scheme 101).

Scheme 101



(*a*) S_2Cl_2, Et_2O (84% yield); (*b*) SCl_2, Et_2O (96% yield)

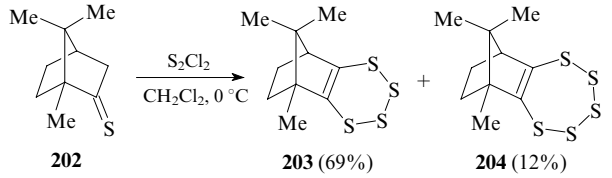
4. Heterocycles with four sulfur atoms

Heterocyclic compounds with four sulfur atoms, obtained with the use of sulfur monochloride, can be divided into two groups — compounds containing four linked sulfur atoms and compounds with two S–S moieties.

Bicyclic thiones are actively studied in the reaction with sulfur monochloride with the aim of producing sulfur-

containing heterocycles. In particular, thiocamphor **202**, containing a free methylene group in the α-position, reacts with S_2Cl_2 to form fused tetrathiane **203**.[131] As a by-product, the authors isolated pentathiepin **204** (Scheme 102). It is worth noting that previously fused 1,2,3,4,5-pentathiepins have been obtained as major products of analogous transformations (see Section III.5).

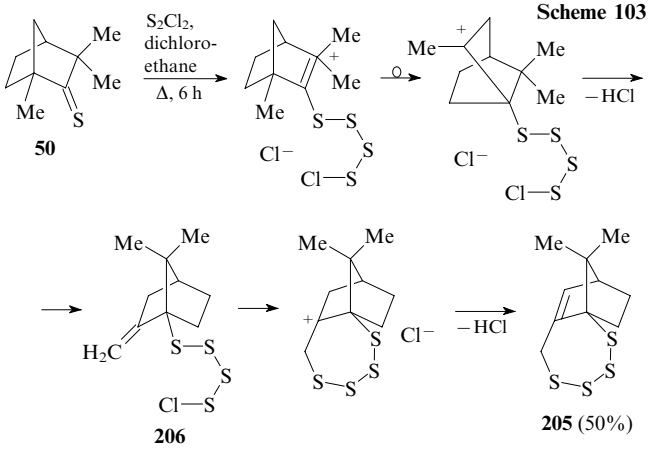
Scheme 102



202 **203** (69%) **204** (12%)

The reaction of sulfur monochloride with thioketone **50**, in which the methylene unit nearest to the thione group contains two methyl groups, leads to thiepane **205**. This product is a result of a complex sequence of transformations, involving the S_2Cl_2 attack, the Wagner–Meerwein rearrangement and cyclization of compound **206** to tetrathiepane (Scheme 103).[50]

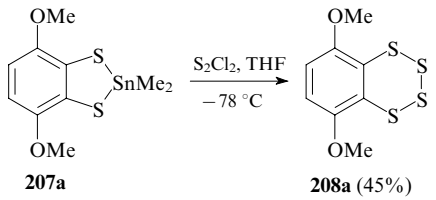
Scheme 103



50 **206** **205** (50%)

Benzodithiastannoles have been early known as promising precursors in synthesis of fused 1,2,3,4,5-pentathiepins; three sulfur atoms are introduced with the use of sulfur monochloride (see Section III.3). Recently, it has been shown that carrying out the reaction at low temperature in tetrahydrofuran allows the reaction to be stopped after the formation of benzo-1,2,3,4-tetrathiane. In particular, the reaction of 4,4-dimethoxy-2,2-dimethyl-1,3,2-benzodithiastannole (**207a**) with S_2Cl_2 leads to tetrathiine **208a** in moderate yield (Scheme 104).[132]

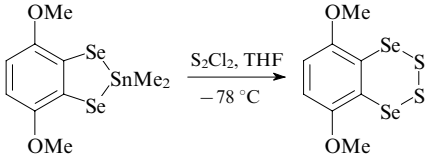
Scheme 104



207a **208a** (45%)

It should be noted that an analogous reaction has also been carried out for the diselenium analogue of compound **207** — benzo-1,3,2-diselenastannole **209**; however, the yield of corresponding benzo-2,3,1,4-dithiadiselenin **210** is considerably lower — 24% (Scheme 105).[133]

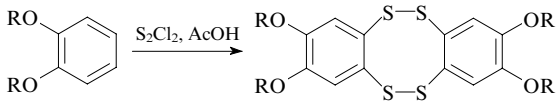
Scheme 105



209 **210** (24%)

1,2,5,6-Tetrathiocines **211**, containing four sulfur atoms arranged as two S_2 pairs, have been synthesized in high yields from activated aromatic compounds — 1,2-dialkyloxybenzenes. The reaction with sulfur monochloride is carried out in acetic acid (Scheme 106).[134, 135]

Scheme 106

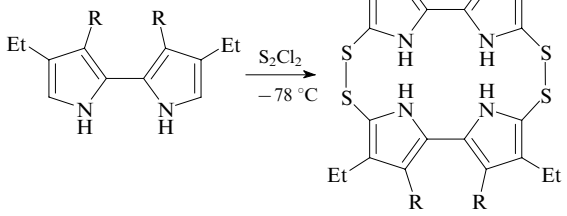


211 (65%–86%)

R = Me, Et, Pr^i, *etc.*

The reaction of bi- and bispyrroles containing unoccupied ,α,α′-positions with sulfur monochloride in an argon atmosphere at −78 °C leads to S_2-bridged oligopyrrole macrocyclic compounds **212** and **213** (Schemes 107, 108).[136]

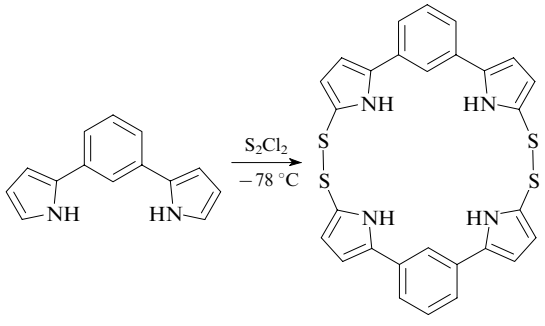
Scheme 107



212 (34%)

R = Me, Et

Scheme 108



213 (27%)

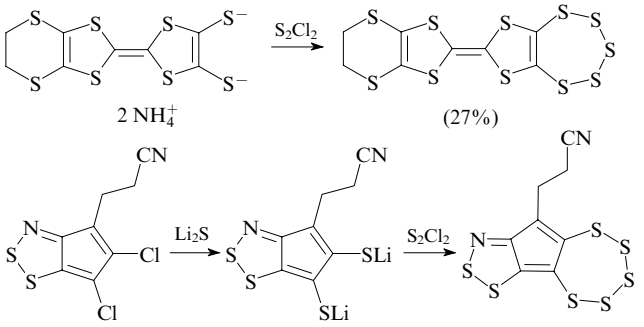
It should be noted that, under analogous conditions, sulfur monochloride can form systems containing S_3 bridges (see Section III.6). These systems are analogues of oligopyrrole macrocycles linked by carbon-containing bridges, which play an important role as ligands for formation of complexes with cations or receptors for anion recognition.

5. Heterocycles with five introduced sulfur atoms

a. 1,2,3,4,5-Pentathiepins

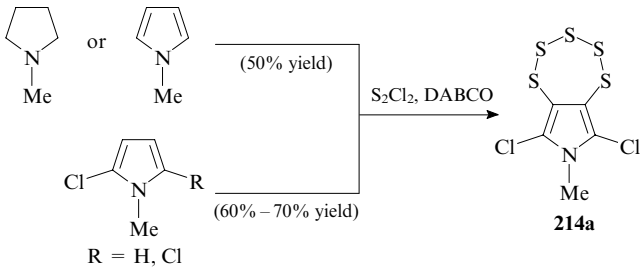
The simplest method of synthesis of fused 1,2,3,4,5-pentathiepins is based on the reaction of 1,2-dithioles or their salts with sulfur monochloride. This method was discovered more than 30 years ago and has been actively used until the beginning of the 21st century. Examples of this reaction, including that where dithiolates were obtained *in situ*, are shown in Scheme 109.[118, 137]

Scheme 109



An uncommon method of synthesis of pentathiepins fused with heterocycles was discovered in the early 2000s by Rees and co-workers.[12] The reaction of nucleophilic heterocyclic compounds, such as pyrroles and thiophene and their tetrahydro derivatives, with sulfur monochloride and a base (as a rule, DABCO) has been proposed as a simple method of one-pot synthesis of fused mono- and bis(pentathiepins).[138] It has been found that *N*-methylpyrrole and its 2-chloro and 2,5-dichloro derivatives form the same dichloropentathiepin **214a** (Scheme 110).

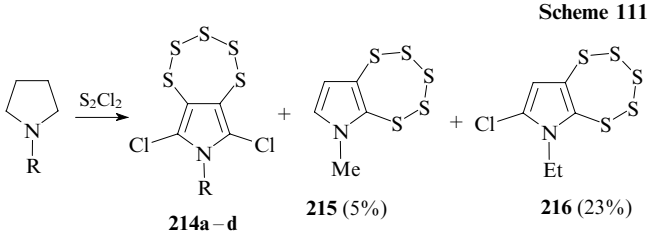
Scheme 110



Easily available *N*-methyl-, *N*-ethyl-, *N*-isopropyl- and *N*-*tert*-butylpyrrolidines form corresponding *N*-alkyldichloropentathiepinopyrroles **214** in low to moderate yields (16% – 31%). A small amount (5%) of compound **215** with the pentathiepin ring fused to the pyrrole 2,3-bond has been isolated as a by-product (Scheme 111).

N-Ethylpyrrolidine affords, in higher yield, analogous product **216** but chlorinated at the free α-position.

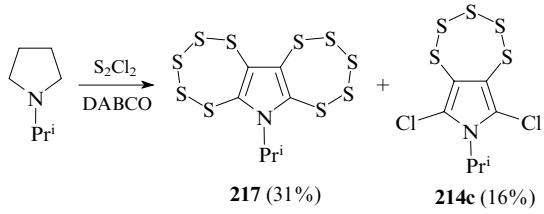
Scheme 111



241: R = Me (**a**, 31% yield), Et (**b**, 29%), Pr^i (**c**, 16%), Bu^t (**d**, 31%)

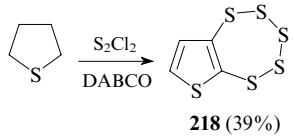
N-Isopropylpyrrolidine in this reaction unexpectedly forms a mixture of two pentathiepins; the isopropyl group, usually reactive under similar conditions, remains intact. One of the products is dichloropentathiepin **214c** and the other is bis(pentathiepin) **217**, which is the first and, until now, single example of a compound containing two pentathiepin rings in the same molecule (Scheme 112).[139, 140]

Scheme 112



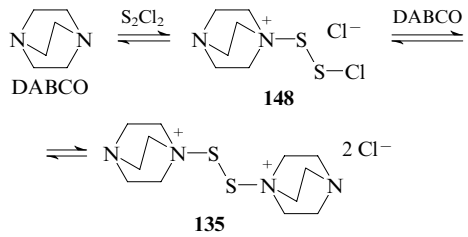
Thiophene reacts with S_2Cl_2 in the presence of DABCO to form a mixture of oligomers that do not contain pentathiepin rings. Tetrahydrothiophene gives pentathiepin **218** in 39% yield with a decrease in the amount of the S_2Cl_2 – DABCO system as compared with the commonly used one (Scheme 113). This fact enables the suggestion that thienopentathiepin **218** can decompose under the action of an excess of reactants to give a mixture of oligomers. This has been proved by the reaction of product **218** with a mixture of S_2Cl_2 and DABCO.

Scheme 113



Other aromatic heterocycles, such as indoles and furan, do not form pentathiepin derivatives under analogous conditions. All these data indicate that if the initial compound has several sites for condensation of the pentathiepin ring, reactions can be not regioselective and that the processes are sensitive to the nature of a heterocycle and conditions applied.[138, 141] It has been found that mixtures of S_2Cl_2 and DABCO combined in definite ratios and kept in chloroform at 0 °C for 48 h or at room temperature for 1 h form reactive salts **148** (at the ratio S_2Cl_2 : DABCO = 1 : 1) and **135** (S_2Cl_2 : DABCO = 1 : 2) (Scheme 114).[141]

Scheme 114

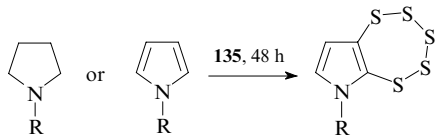


It has been suggested that these salts have different chemical properties: salt **148** can be a potential source of Cl^+ and $Cl-S-S^+$ species and can exhibit chlorinating and sulfurating properties, whereas salt **35** exhibits only sulfonating ability.

Treatment of *N*-alkylpyrrolidines or -pyrroles, as well as -indoles, with a fivefold excess of salt **135** in chloroform at

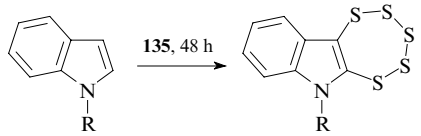
room temperature for 48 h regioselectively leads to *N*-alkyl-1,2,3,4,5-pentathiepinopyrroles **219** and -indoles **220**, respectively (Scheme 115).[141]

Scheme 115



219 (29%–61%)

R = Me, Et, Pr^i, Bu^t



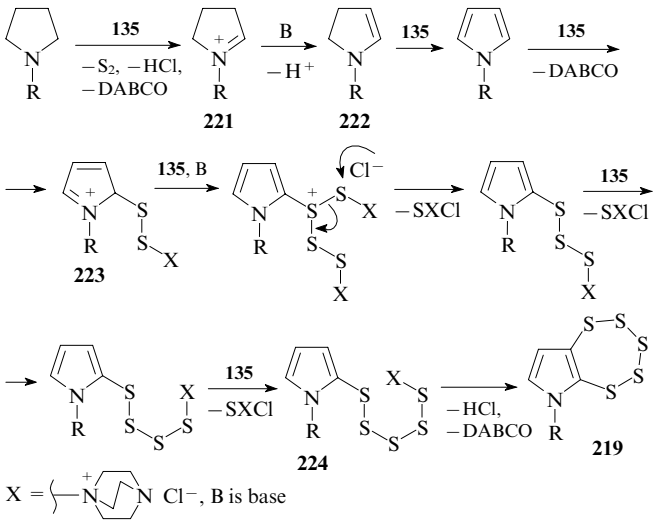
220 (51%–62%)

R = Me, Et

Reactions of salt **135** with other heterocyclic compounds have been studied. Furan, thiophene and benzo[*b*]thiophene do not react with salt **135**. Tetrahydrothiophene forms, under these conditions, pentathiepin **218** in the highest yield described in the literature. Thus, the use of salt **135** makes the reaction more selective than the use of mixtures of S_2Cl_2 and DABCO.

In the reaction mechanism suggested by the authors and considered for *N*-methylpyrrolidine as an example, the key stages are aromatization of a saturated heterocycle and formation of the pentathiepin ring in the α-position. The first stage of this transformation is the oxidation of *N*-methylpyrrolidine with salt **135** to iminium salt **221**, which then reacts with a base to form enamine **222** (Scheme 116).[72]

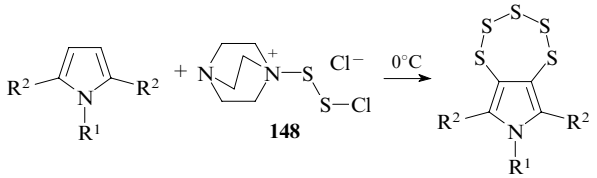
Scheme 116



Repetition of this process leads to *N*-methylpyrrole. The next stage is electrophilic substitution under the action of salt **135** at the 2-position of the heterocycle to form salt **223**. It was assumed that then the addition of salt **135** to the S_nX chain and elimination of SXCl leads to the $S_{(n+1)}X$ chain. Eventually, the substituent in pyrroles **224** is converted into the thermodynamically stable pentathiepin ring.

The reaction of salt **148** with *N*-alkyl- and *N*-phenyl-2,5-disubstituted pyrroles at 0 °C also gives corresponding pentathiepins **147** in higher yields than the reactions with mixtures of S_2Cl_2 and DABCO (Scheme 117).

Scheme 117

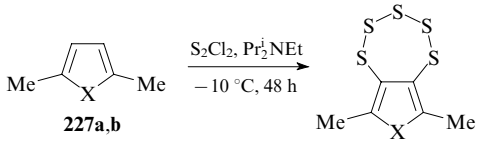


147 (36%–62%)

R^1 = Me, Ph; R^2 = Me, Et, Pr^n, Pr^i, Bn

Even milder conditions have been used for synthesis of thienopentathiepin **225** and pentathiepinofuran **226** from corresponding heterocycles **227a**,**b**.[142] The latter react with sulfur monochloride and diisopropylethylamine on cooling to −10 °C to form the corresponding pentathiepins, although in low yield (Scheme 118).

Scheme 118



227a,**b** → **225**, **226**

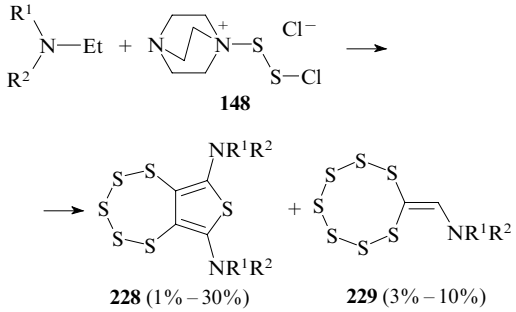
X = S (**227a**, **225**; 13% yield), O (**227b**, **226**; 11%)

The above transformations are complex cascade reactions, which enable the synthesis of polycyclic pentathiepins, their chlorinated derivatives and rearrangement products from simple saturated and aromatic heterocycles. All this clearly illustrates the diverse reactivity of sulfur monochloride and its salts with bases.

Extraordinary results were obtained by the reaction of salt **148** with triethylamine, which is used in many reactions as an 'inert' base.[143] From the reaction mass, thienopentathiepin **228** (R^1 = R^2 = Et, 30%) and heptathiocane **229** (R^1 = R^2 = Et, 10%) were isolated. Studies have shown that analogous transformations occur also for other tertiary *N*-ethylamines, but the products are obtained in lower yield. It is worth noting that, despite low yields, this uncommon reaction enables the one-pot synthesis of unique thienopentathiepins **228** and heptathiocanes **229** from inexpensive and easily available reactants (Scheme 119).

An important specific feature of molecule **228** is that the thiophene ring is formed from two ethyl groups and the C–C bond is constructed from two formally nonactivated methyl groups; the pentathiepin ring is evidently annelated

Scheme 119



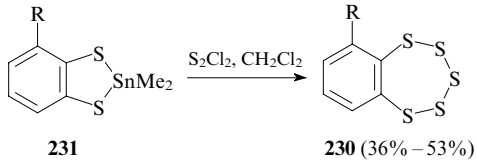
228 (1%–30%) **229** (3%–10%)

R^1 = Et: R^2 = Pr^n, Bn; R^1 = R^2 = Et, Pr^i, Bn; R^1–R^2 = $(CH_2)_4$

to the thiophene ring by a mechanism analogous to the above one (see Scheme 116).

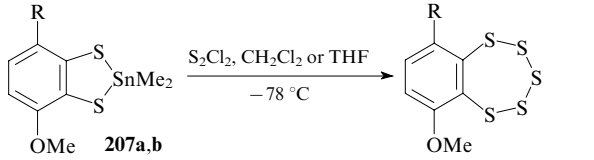
In recent years, Japanese researchers have paid much attention to the development of approaches to the synthesis of benzo-1,2,3,4,5-pentathiepins based on the reaction of 1,3,2-benzodithiastannoles with sulfur monochloride.[144] The idea of using these heterocycles is caused by the necessity to protect unstable 1,2-dithiolobenzenes, which have been widely used for synthesis of pentathiepins.[139] Although the yields of pentathiepins **230** and **208a**,**b** from dithiastannoles **231** and **207a**,**b** are not always high, this reaction attracts attention by the possibility of carrying out the process at low temperature (down to −78 °C) (Scheme 120).[132, 145–147]

Scheme 120



231 **230** (36%–53%)

R = Ph, 2-MeC$_6$H$_4$, Naph

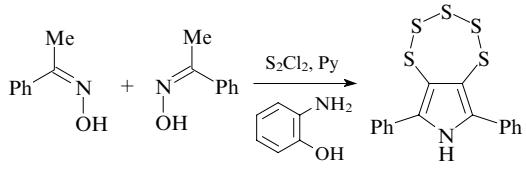


207a,**b** **208a**,**b** (82%–95%)

R = OMe (**a**), Et (**b**)

Pyrrolopentathiepin **232** was unexpectedly isolated as a by-product in the reaction of acetophenone oxime with sulfur monochloride in the presence of pyridine and *o*-aminophenol (Scheme 121).[83] A possible mechanism of formation of this product is described in the original paper.

Scheme 121



232 (2%)

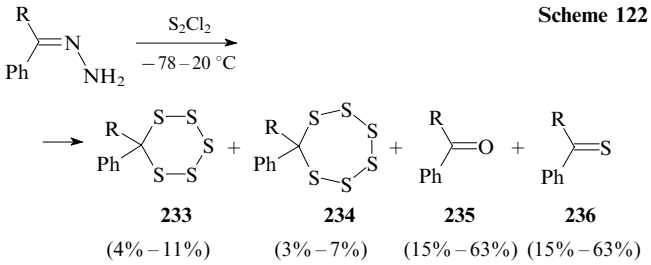
Sulfur monochloride was also successfully used for synthesis of poly(*N*-methylpyrrole) fused with pentathiepin rings from the corresponding pyrrole polymer.[148]

b. Other heterocycles

The reaction of 1-adamantyl phenyl ketone, pivalophenone and benzophenone hydrazones with sulfur monochloride leads to pentathianes **233** and hexathianes **234** as by-products; the major reaction products are corresponding ketones **235** and thioketones **236** (Scheme 122).[21]

The reaction of dithiadiazocanes **237** with sulfur monochloride affords a new class of macrocyclic polysulfides — 1,2,3,4,5,7-pentathiazocanes **238** in moderate to high yield.[149, 150] The NMR spectra of the reaction mixture enables the suggestion that the key intermediate product of this reaction is symmetric dithia dication **239**, which decomposes to dithiazole. The latter is then sulfurated by

Scheme 122



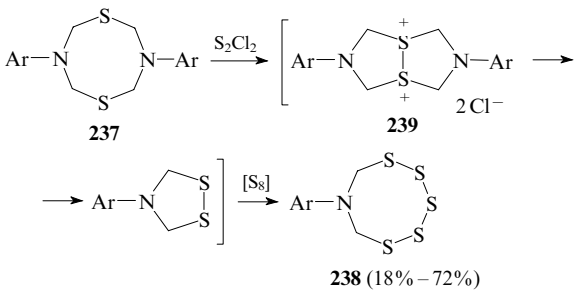
233 **234** **235** **236**

(4%–11%) (3%–7%) (15%–63%) (15%–63%)

R = Ad, Bu^t, Ph

nucleophilic species that form from elemental sulfur (Scheme 123).

Scheme 123



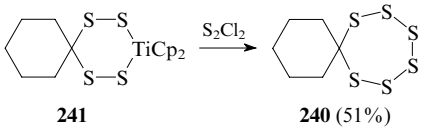
237 **239** **238** (18%–72%)

Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$

6. Heterocycles with six or more sulfur atoms

The previously undescribed polysulfur-containing heterocyclic compound **240** has been synthesized by the reaction of titanocene complex **241** with sulfur monochloride (Scheme 124).[151]

Scheme 124

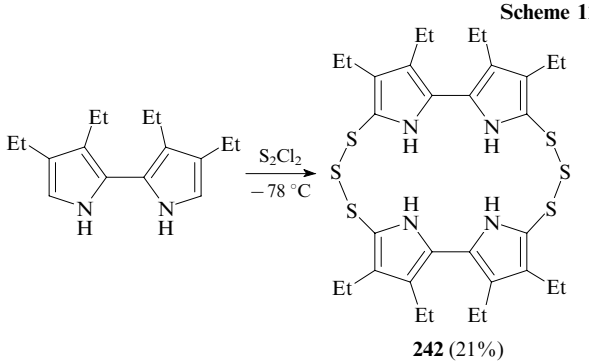


241 **240** (51%)

The reaction of 3,3′,4,4′-tetraethyl-2,2′-bipyrrole, containing hydrogen atoms in the α,α′-positions of the heterocycle, with sulfur monochloride under argon at −78 °C leads to macrocycle **242**, in which two bipyrrole moieties are linked by two chains each of three sulfur atoms (Scheme 125).[136]

The mechanism of this transformation has not been reported; however, it should be noted that other pyrroles

Scheme 125

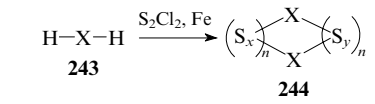


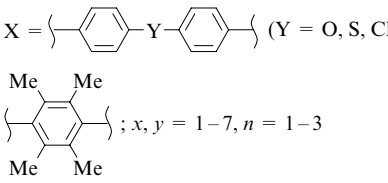
242 (21%)

react with S_2Cl_2 under the same conditions to form products with chains of two sulfur atoms (see Section III.4).

Macrocyclic oligomers are of interest as initial compounds for synthesis of highly efficient aromatic macromolecules by ring opening polymerization. Upon slow addition of diphenyl derivatives **243** to dilute solutions of sulfur monochloride in the presence of iron powder as a catalyst, mixtures of oligomers **244** are formed in quantitative yield.[152–154] MALDI-TOF mass spectrometry demonstrates that the macrocycle contains from two to six repeating units, each of them containing from one to seven sulfur atoms (Scheme 126).

Scheme 126





* * *

The transformations considered in this review demonstrate that sulfur monochloride is an important reagent for synthesis of both acyclic and heterocyclic compounds containing a different number of sulfur atoms. An important and unique feature of this reagent is that it can introduce not only two sulfur atoms, as expected from its formula, but also one, three, four, five and even more sulfur atoms. The structure of the products is essentially dictated by their stability. Recent progress in applying sulfur monochloride is based on its ability to form salts with organic bases that exhibit quite different chemical properties. This enables the targeted synthesis of compounds with a definite number of introduced sulfur atoms. As required by modern materials chemistry, the exact choice of reaction conditions — temperature, solvent, catalyst and concomitant base — is important for synthesis of sulfur-containing heterocyclic compounds of desired structure.

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