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SYNTHESES OF TETRAHETEROFULVALENES AND OF VINYLENE TRIHETEROCARBONATES—STRATEGY AND PRACTICE

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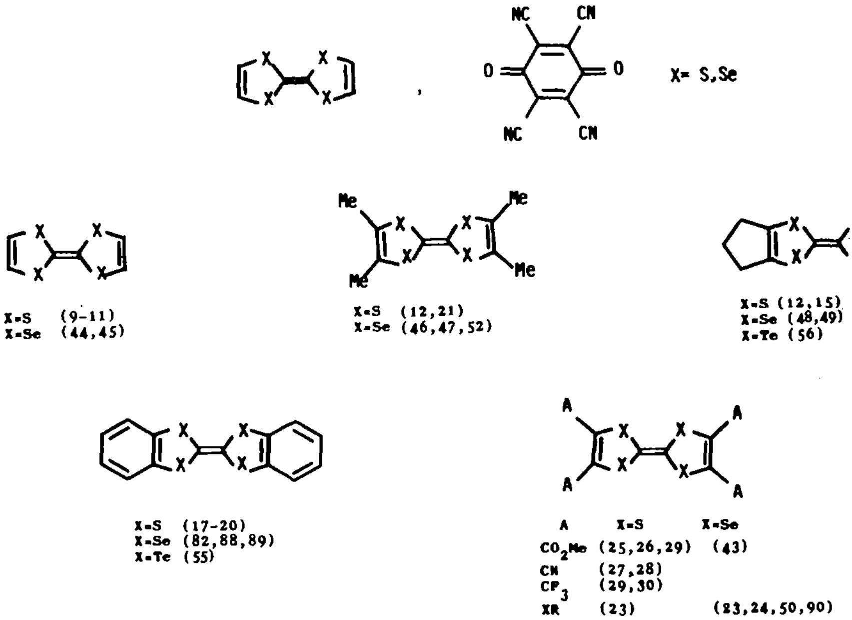
CONTENTS

I. SYNTHESIS OF TETRAHETEROFULVALENES

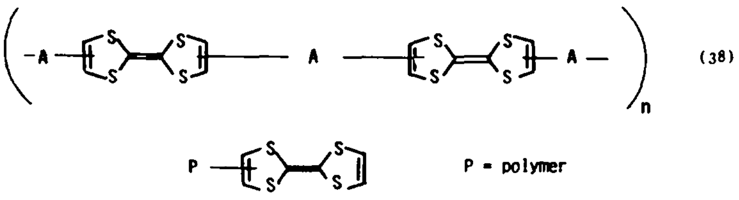
The synthesis of bis-1,3-dithiolium chloride[1] and of the salt of tetrathiafulvalene and tetracyanoquinodimethane[2] (TCNQ) and the discovery of their exceptional electrical conductivity[1–4] has encouraged research in the synthesis of organic compounds which have measurable electrical properties.

Due to this increased interest, many compounds related to tetrathiafulvalenes have been synthesized during the last decade[5,6] (Schemes 1–3), and the electrical and optical properties of their complexes with electron-deficient compounds have been studied.[5–8] (Reference numbers in parentheses are indicated on the schemes.)

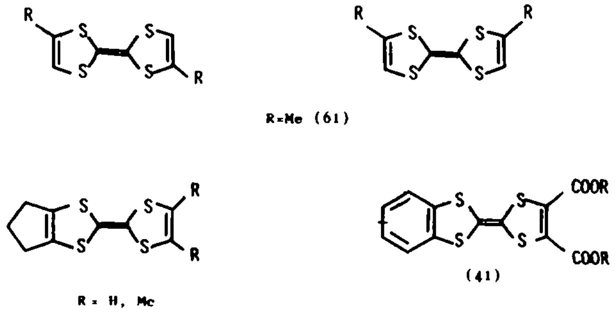
In addition to the original methods for the synthesis of tetrathiafulvalene (TTF),[9–12] there



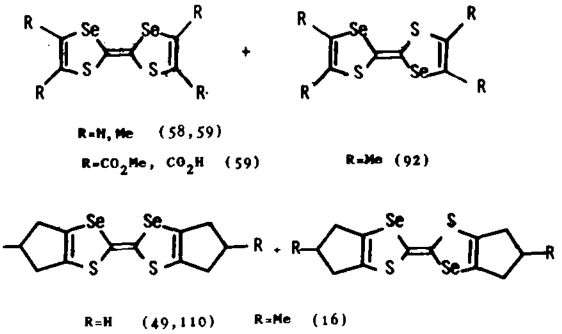
Scheme 1(a).



Scheme 1(b).



Scheme 2.



Scheme 3.

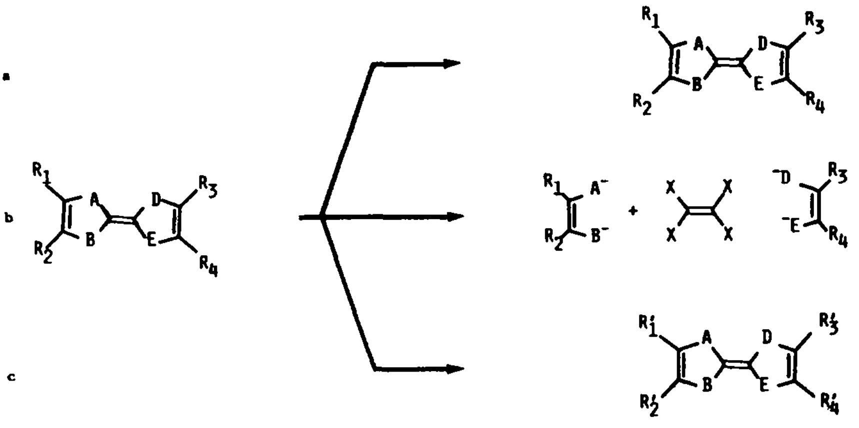
also exists the preparation of analogues where all the hydrogens are substituted by alkyl groups (such as tetramethylthiafulvalene),[12,13] cycloalkyl,[12,14–16] aryl,[12,15–21] (including dibenzotetrathiafulvalene),[17–20,22] or thioalkyl[23,24] groups as well as those possessing electron-withdrawing groups such as tetracarbomethoxy-,[12,25,26] tetracyano-[27,28] or tetratrifluoromethyl-[29,30] tetrathiafulvalene (Scheme 1).

A series of unsymmetrically substituted analogues of TTF has also been described [11,31–36] (Scheme 2), in particular, those being part of, or attached to, a polymeric system[37–40] (Scheme 1).

Originally, the synthetic methods available led to a mixture of all possible isomers. As a consequence,[32–34,41,42] the purification of products often necessitated fastidious separations based on solubility differences. More recently, methods have been developed which permit the selective synthesis of certain compounds[19,20,33,35] unsymmetrical about the carbon–carbon bond.

Research has not been confined only to tetrathiafulvalenic derivatives; tetraselenated[21,23,43–54] and tetratellurated[55–57] analogues have also been prepared (Scheme 1), as well as mixed derivatives containing sulfur and selenium[49,58,59] atoms in the same compound (Scheme 3). All of these derivatives have been converted into complexes, the physical properties of which have been studied intensively.

The goal of this report is to describe the different methods for the synthesis of these molecules, showing the advantages and the limitations as well as presenting the strategies used in these syntheses.



Scheme 4.

The methods of synthesis of tetrathiafulvalenes and their selenated and tellurated analogues can be classified in three general categories. The last step involves:

(1) the formation of the tetraheterosubstituted π-bond (Scheme 4(a));

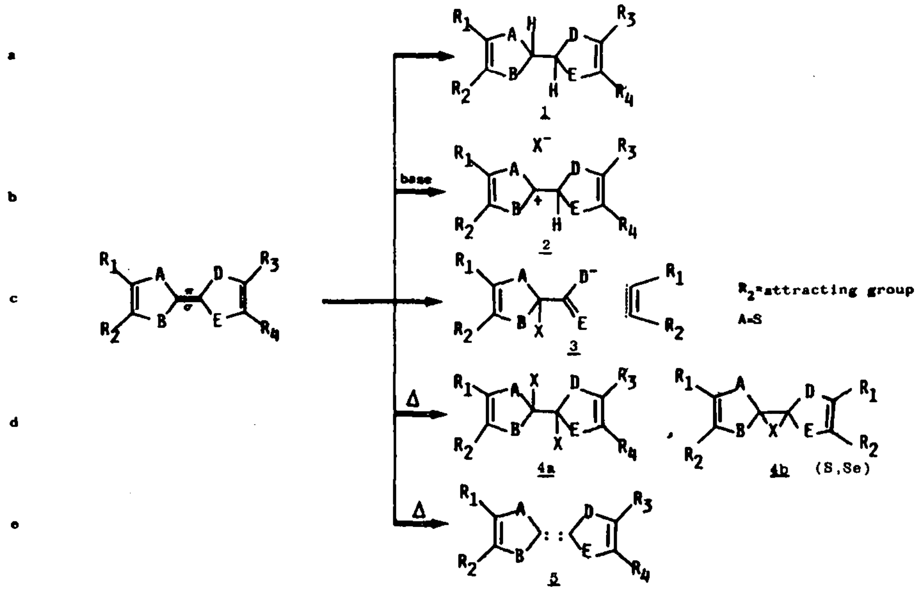
(2) the substitution of the four halogens of tetrachloroethylene by appropriately substituted thiolates, selenolates or tellurolates (Scheme 4(b));

(3) the functionalization of tetraheterofulvalene or side chain modification of its analogues (Scheme 4(c)).

1. SYNTHESES INVOLVING FORMATION OF THE TETRAHETEROSUBSTITUTED BOND IN THE FINAL STEP

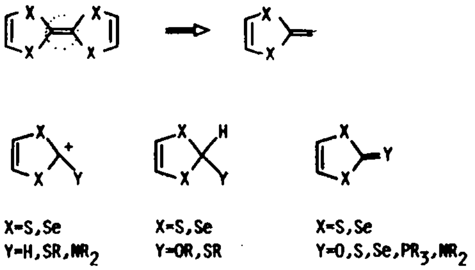
These methods, by far the most numerous and the most important, are shown in Scheme 5. The π-bond is formed via an elimination reaction involving either, two protons (electrochemical oxidation) (Scheme 5(a)), one proton (Scheme 5(b)) or one or two heteroatoms (Schemes 5(c) and (d)). In addition, the σ- and π-bonds can be formed simultaneously by a coupling reaction of two carbenes (Scheme 5(e)).

Therefore, it is important to possess adequate methods of synthesis of precursors 1–5. In the majority of cases, this involves coupling of a 1,3-dihetero-4,5-cyclopentene-2-ylid (Scheme 6) arising



Scheme 5.

from the 1,3-dithiols (electrochemical coupling), the 1,3-dithiolium salts, heterosubstituted in the 2-position (coupling in the presence of base or electrochemically), the 2-alkoxy-1,3-dithiols (thermal coupling) or the 2-oxo-, 2-thioxo-, 2-selenoxo- and 2-imino-1,3-dithiols (coupling via phosphines). These reactions have often been extended to analogues possessing a selenium atom in the 1- and/or 3-position of the heterocycle.

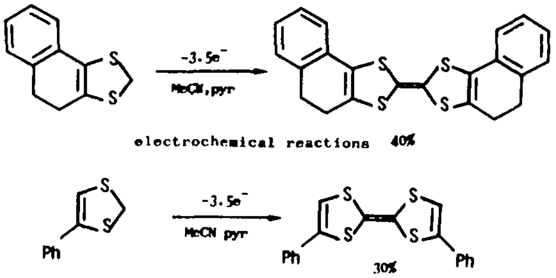


Scheme 6.

These derivatives are easily interconvertible and play a primary role in the syntheses of tetrathia- and tetraselenofulvalenes. A separate section has therefore been dedicated to the description of their syntheses (Part II).

1.1. *Syntheses of tetrathiafulvalenes involving the oxidation of a dihydrotetrathiafulvalene*

Recently, it has been shown[31] that 1,3-dithiols are oxidatively dimerized to tetrathiafulvalenes by an electrochemical route (Scheme 7).



Scheme 7.[31]

The reaction has only been described for 1,3-dithiols with an aryl substituent in the 4-position. It is only effective in the presence of pyridine. The authors propose that the anodic oxidation of the heterocycle leads to a radical cation, which is then deprotonated by the pyridine to give a 1,3-dithiolium radical in the 2-position. This dimerizes to the dihydrotetrathiafulvalene which is then oxidized at the anode to provide the tetrathiafulvalene.

1.2. *Synthesis of tetrathia- and tetraselenofulvalenes via elimination of a proton in the last step*

The process, which allows access to heterofulvalenes according to this route, involves the reaction of a carbene or of a phosphorus ylide on a 1,3-dithiolium or a 1,3-diselenolium salt possessing a hydrogen at carbon-2. The adduct (Scheme 8) is usually transformed into the heterofulvalene by an amine, which acts as a base. The 1,3-dithiolium salts, as well as their diseleno or sulfur-seleno analogues, play a major role in these approaches.

1.2.1. *Synthesis of* 1,3-*dithiolium,* 1,3-*diselenolium and* 1,3-*selenothiolium salts possessing a hydrogen in the* 2-*position*†

1.2.1.1. *Via alkylation of* 2-*thioxo*-1,3-*dithiol salts.* 1,3-Dithiolium salts, unsubstituted in the

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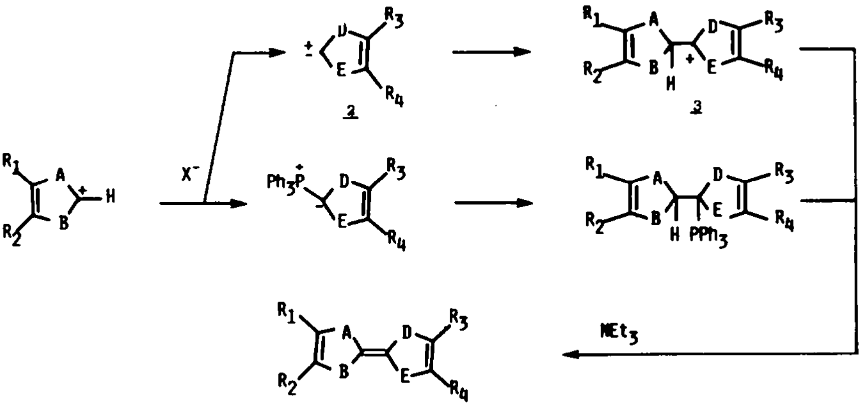
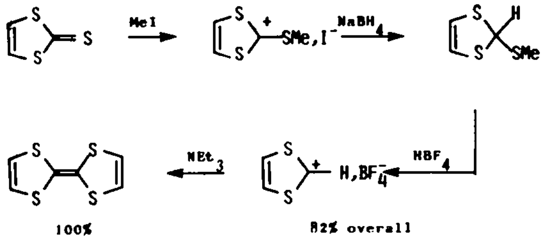
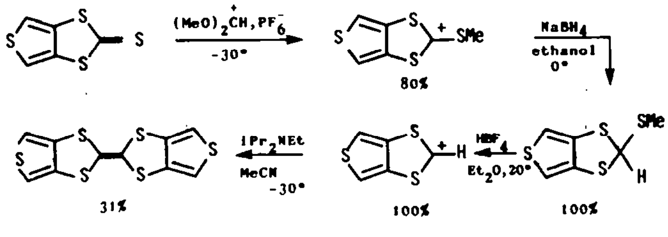
† For leading references on the synthesis and on the stability of such species see: L. Hevesi, *The Chemistry of Organic Selenium and Tellurium Compounds* (Edited by S. Patai and Z. Rappoport). Wiley, U.K. (1986), in press.



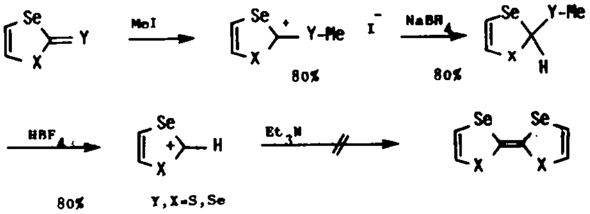
Scheme 8.



Scheme 9.[9]



Scheme 10.[60,64]



Scheme 11.[58,62]

2-position, are prepared in excellent yield from 2-thioxo-1,3-dithiols[9,10,15,32,33,60–64] or from 2-selenoxo-1,3-dithiols[62] by a series of reactions involving (Schemes 9–11):

(1) the synthesis of 2-thioalkyl- or 2-selenoalkyl-1,3-dithiolium salts via alkylation of the thione or selone group by an alkyl halide;

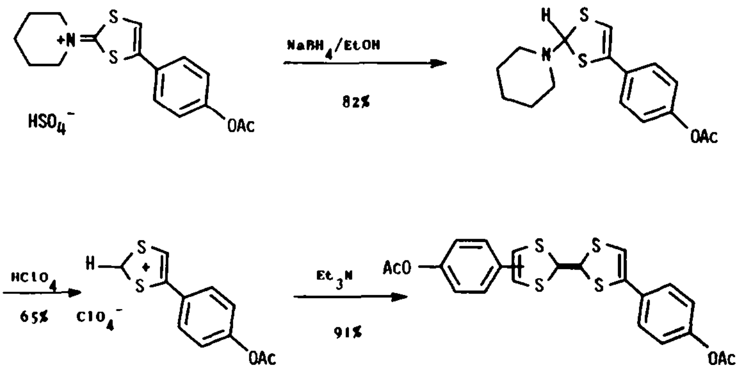
(2) the reduction of these salts by sodium borohydride, which generates the 2-alkylthio- or 2-alkylseleno-1,3-dithiols;

(3) the treatment of these derivatives with a strong acid, generally fluoroboric acid, which leads to 1,3-dithiolium salts unsubstituted in the 2-position. Fluoroboric acid is often preferred to sulfuric acid, which produces hygroscopic salts,[5] or to perchloric acid, which can lead to explosive salts.[5]

This method calls for additional comments. For example, the alkylation step (Step 1) is much easier with the selone than with the thione, if the rest of the molecule remains the same. It does not pose a major problem when the heterocycle is unsubstituted,[62] or contains alkyl groups[15,32,33,65] in the 4,5-position, but becomes very difficult when electron-withdrawing groups are placed in the same position.[26,66]

This series of reactions has been successfully applied to the synthesis of 1,3-selenolium salts from 2-selenoxo-1,3-diselenols[62] and of 1,3-selenothiolium salts from 2-thioxo-1,3-selenothiolium salts[62] (Scheme 11).

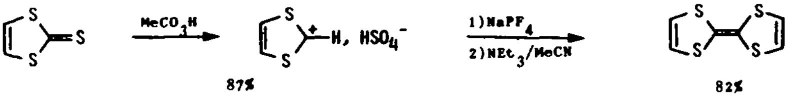
1.2.1.2. *Via 2-iminium-1,3-dithiol salts.* Alternatively, 1,3-dithiolium salts unsubstituted in the 2-position are obtained[5,26] from 2-N,N-dialkylamino-1,3-dithiolium salts by reduction of the latter with sodium borohydride and reaction of the resulting N,N-dialkylamino-1,3-dithiols with a strong acid (Scheme 12). This method avoids the previously mentioned alkylation step when the thione or the selone are utilized as starting materials and gives dithiolium salts which are unsubstituted in the 2-position and are inaccessible by other routes.



Scheme 12.[24]

1.2.1.3. *Via 2-thioxo-1,3-dithiols by oxidation.* 1,3-Dithiolium salts possessing a hydrogen in the 2-position are easily obtained in one step by oxidation of a 2-thioxo-1,3-dithiol by a peracid[13,16,37,66–69] or H_2O_2 in acetic acid[70] (Schemes 13 and 14). The presence of alkyl groups in position 4 or 5 does not seem to interfere with the course of the reaction.[37,68] On the other hand, the presence of electron-withdrawing groups in these positions renders the reaction particularly difficult,[66] or will even totally inhibit the reaction, as is the case with 4,5-dicyano-2-thioxo-1,3-dithiol (Scheme 15).

This method has a disadvantage when compared to the others in that it cannot be used to prepare

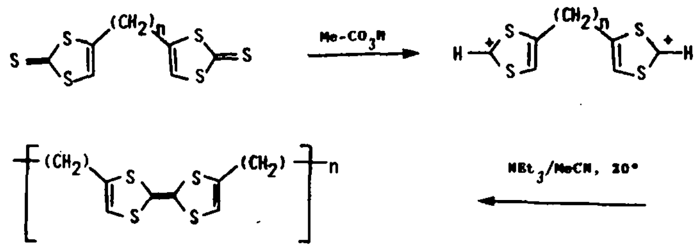


Scheme 13.[11]

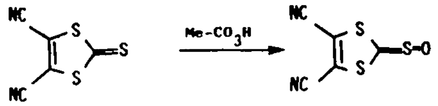
1,3-diselenolium salts from 2-thioxo- or 2-selenoxo-1,3-diselenol,[2,45] or 1,3-selenothiolium[58] from 2-thioxo- or 2-selenoxo-1-seleno-3-thiol (Scheme 16).

1.2.2. *Synthesis of tetrathia- and tetraselenofulvalenes by reaction of 1,3-dithiolium salts with base*

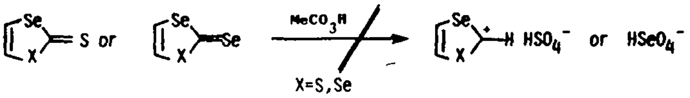
1.2.2.1. *Reaction of base with 1,3-dithiolium salts.* Treatment of 1,3-dithiolium salts dissolved in acetonitrile with an excess of a tertiary amine (such as ethyldiisopropylamine or triethylamine) leads directly to tetrathiafulvalenes[9,10,15,32,33,37,42,60,64,68] (Schemes 9, 10, 12 and 13). Given the requisite starting dithiolium salt, this reaction can be used for the preparation of a series of tetrathiafulvalenes with a variety of substituents on the ring. A mixture of *cis* and *trans* stereoisomers is obtained if the dithiolium salt is unsymmetrical,[37,42,71,72] whereas reaction of base with a mixture of two different symmetrical 1,3-dithiolium salts gives a mixture, often purifiable, of the three possible tetrathiafulvalenes (Scheme 17).



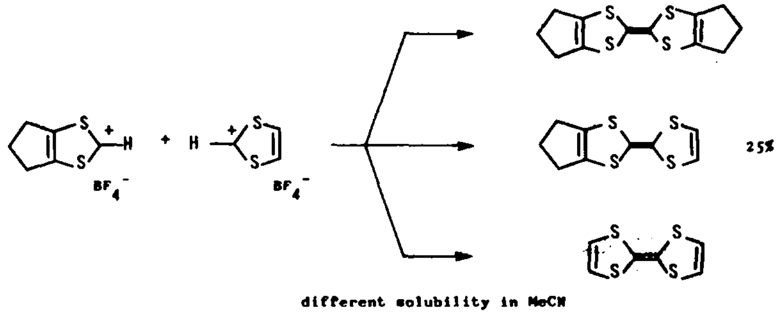
Scheme 14.[37]



Scheme 15.[66]



Scheme 16.[45,58,62]



Scheme 17.[32-34]

Unfortunately this reaction is not applicable to 1,3-diselenolium salts or to 1,3-selenothiolium salts and as a consequence, the tetraselenofulvalenes[2,45] or the heterofulvalenes (S, Se)[58] are not accessible by this method.

The mechanism of these reactions has not been clearly established. From the work of Prinzbach and co-workers,[42,73] it is certain that the proton at C-2 of the 1,3-dithiolium salts is highly acidic. It is assumed that under basic conditions, the 1,3-dithiolium salt at least partially forms the corresponding carbene (**2**, Scheme 8) and that the latter couples with the remaining dithiolium salt to give the intermediate **3**, which is the immediate precursor of the tetrathiafulvalene. The tetrathiafulvalene may also arise from dimerization of the carbene, but in general, although this type of reaction is less probable in solution, one cannot definitely exclude it because the lifetime of such carbenes is particularly long.[29,42]

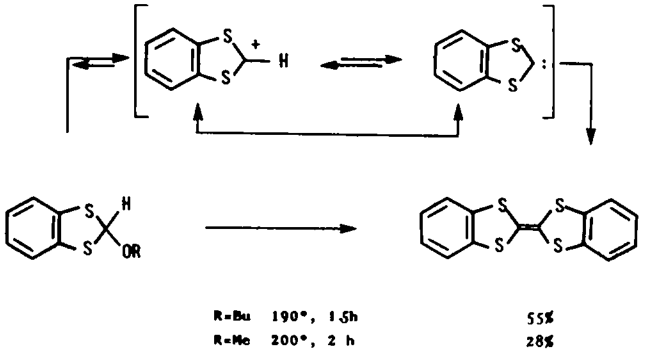
1.2.2.2. *Basic treatment of dithiolium salts formed* in situ. The reactions described in the preceding paragraph can be related to the following:

(1) Pyrolysis[18] of a 2-alkoxy-1,3-benzodithiol at 200° affords the benzodithiofulvalene. The latter is obtained in 55% yield starting from the derivative containing a butoxy group in the 2-position, but when the 2-butoxy group is replaced by a methoxy[18] or a t-butoxy[18] group the yields are more modest or practically nothing (Scheme 18). Moreover, this reaction has not yet been generalized to other 2-alkoxy-1,3-dithiol derivatives and has only been tried with the benzothiol derivative.

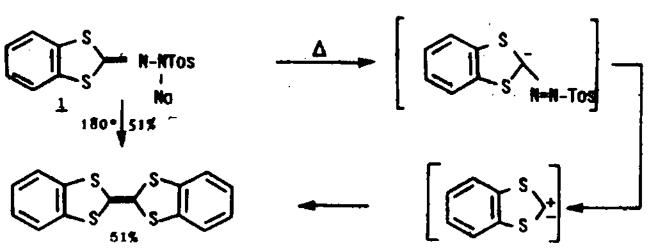
(2) Pyrolysis of 2-imino-1,3-benzodithiol (**1**, Scheme 19) in the presence of one equivalent of sodium methoxide in diglyme at 180°[22] leads to dibenzotetrathiafulvalene in 51% yield.

(3) The reaction of electrophilic[29,30] (Schemes 20–23) or strained[14] (Scheme 24) acetylene derivatives with carbon disulfide.

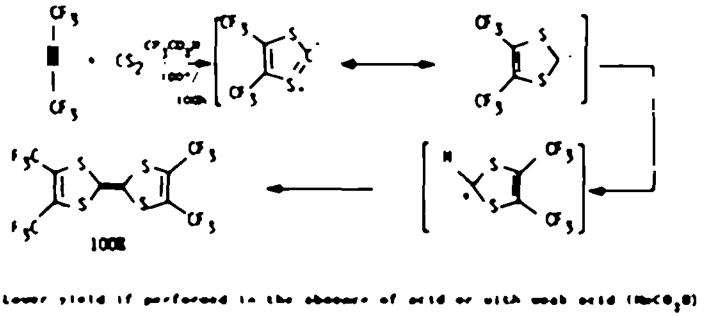
The yields of tetrathiafulvalenes in the first case[29,30] are particularly low when the two moieties are mixed and heated for a long period at 100° in an autoclave.[29,30] Nevertheless, the yields are much better if the reaction is done in the presence of an acid[29,30] (Schemes 20 and 21). This reaction is therefore



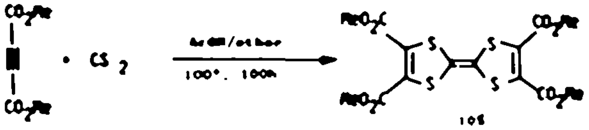
Scheme 18.[18]



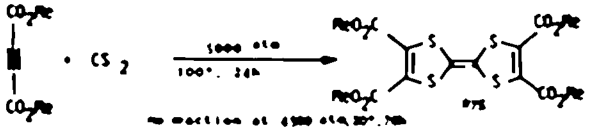
Scheme 19.[22]



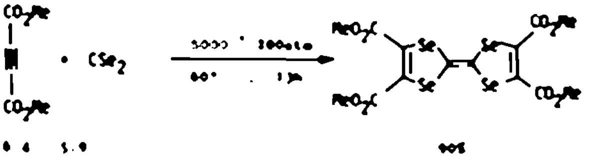
Scheme 20[29,30]



Scheme 21[29]



Scheme 22[31]

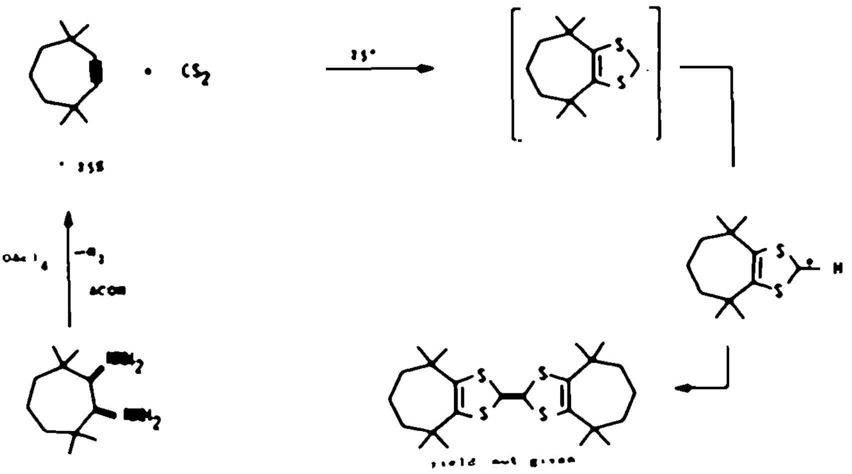


Scheme 23[43]

attractive because it allows one to obtain tetrathiafulvalenes substituted by electron-withdrawing groups. For the first time, this method shows the importance of carbon disulfide and acetylenic derivatives in the synthesis of the general 1,3-dithiolene structure.

The mechanisms of certain reactions described in Section 1.2.2.2 show some analogy to the present discussion. Thus, it is assumed[18] that the 1,3-benzodithiolium salt is formed from the pyrolysis of the 2-alkoxy-1,3-benzodithiol and that it reacts partially with the alkoxide anion, which acts as a base, to form the carbene. The reaction of the latter with the starting dithiolium salt produces the tetrathiafulvalene[29,30] as was already proposed in Section 1.2.2.1 (Scheme 8).

In a similar manner, it can be postulated that the intermediate carbene formed by decomposition of the corresponding tosylhydrazone[22] salt reacts in part with the methanol to form the 1,3-dithiolium salt, which leads to the dibenzotetrathiafulvalene[22] via an identical process as in the preceding case. If



Scheme 24[14]

the pyrolysis reaction is performed in the presence of a large excess of benzyl alcohol, only the 2-benzyloxy-1,3-benzodithiol is isolated in 30% yield.[22] A mechanism involving dimerization of the postulated carbene as an intermediate cannot, however, be excluded. Finally, it is proposed that the carbene, formed by the action of carbon disulfide on the acetylene derivative, is protonated to some extent in the 1,3-dithiolium salt by the added carboxylic acid[29,30] (Scheme 20), or generated[14] in the reaction media (Scheme 24). An identical process to the above, where the acetate would play the role of a base, would also lead to the tetrathiafulvalene.

It should be noted that the need for an acid in the last reaction is a sign in favour of the proposed mechanism and is not in accord with the mechanism involving dimerization of the carbene (at least under the experimental conditions used).[29,30] Nevertheless, this latter mechanism can be operative:[25,43]

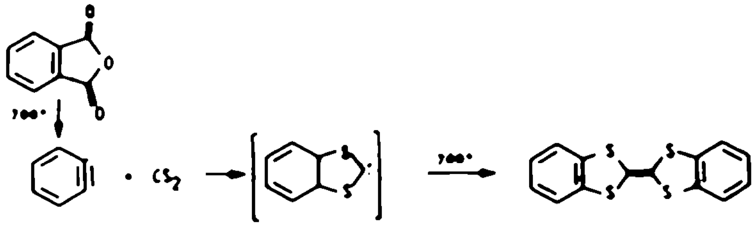
(1) At high pressure (5000 atm). This reaction was successfully used for the synthesis of tetracarbomethoxytetrathiafulvalenes[25] and their tetraselenated[43] analogues (Schemes 22 and 23).

(2) In the gas phase[74] (Scheme 25) (compare Schemes 19 and 25).

1.2.3. *Synthesis of tetraheterofulvalenes involving the elimination of a proton and triphenylphosphine in the final step*

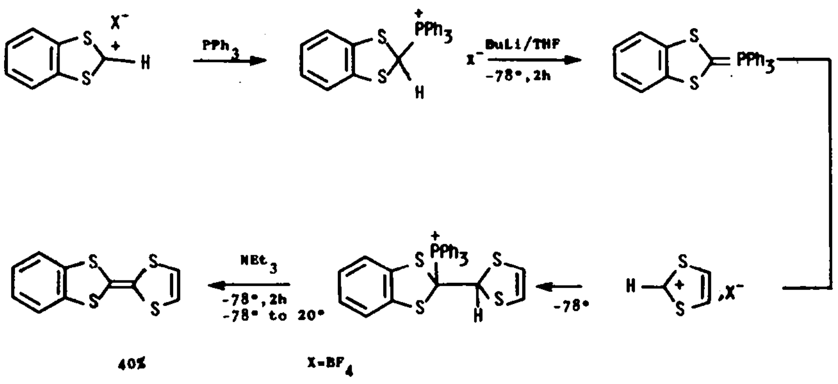
2-Triphenylphosphino-2-metallo-1,3-dithiols react with 1,3-dithiolium salts to give products which give tetrathiafulvalenes on treatment with base (i.e. Et_3N) at low temperature (−78°). This is preferred to the expected classical Wittig reaction involving the same ylide and 2-thioxo- or 2-selenoxo-1,3-dithiols.[35,75]

The phosphorus ylides used in these reactions are very easily accessible by reaction at −78°,



2.58

Scheme 25[74]



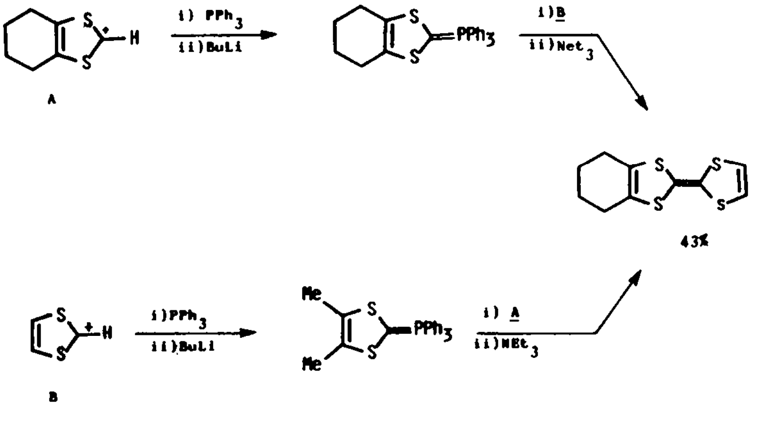
Scheme 26.[35]

between n-BuLi and phosphonium salts which are generated by the action of triphenylphosphine on 1,3-dithiolium salts (Schemes 26 and 27).[35]

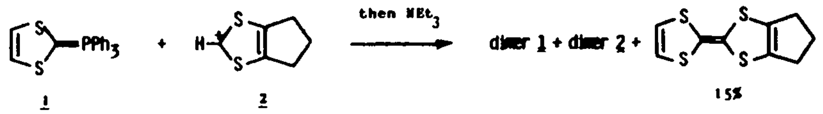
This method permits, for the first time,[35] the selective preparation from variously substituted 1,3-dithiols, of unsymmetrical tetrathiafulvalenes in which the two heterocycles can be substituted by hydrogens, aryl, alkyl, or cycloalkyl groups. Each of these dithiolium salts can be the precursor of the ylide[33,34] (Scheme 28); however, the selectivity mentioned, does not seem to be general, as an exception has recently been noted.[33]

A reaction related to the preceding case can be used to prepare,[11,75] in a one-pot reaction, starting from tributylphosphine, an excess of carbon disulfide and one molar equivalent of methyl propynoate, the tetrathiofulvalene as a mixture of two diastereomers. It has been successfully applied to other electrophilic acetylene derivatives.

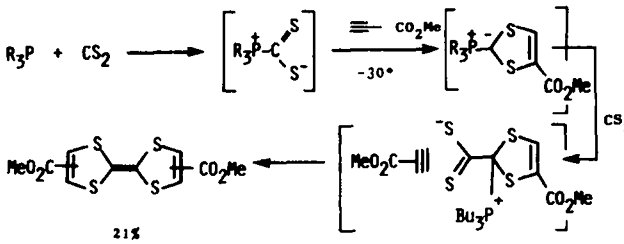
This synthesis takes advantage of the reaction of the CS_2–trialkylphosphine[76] complex with electrophilic acetylenes. The reaction leads to a phosphorus ylide whose presence has been independently proven[75] (in a Wittig type reaction). This ylide is assumed[11] to react with an excess of carbon disulfide and produces the tetrathiafulvalene via the procedure shown in Scheme 29 and related to that shown in Scheme 26.



Scheme 27.[35]



Scheme 28.[33,34]



Scheme 29.[11]

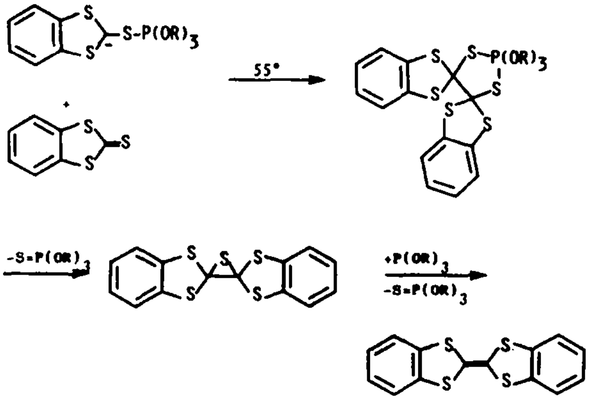
1.3. *Synthesis of tetraheterofulvalenes by elimination of two heterosubstituted entities in the final step*

1.3.1. *Deoxygenation of 2-oxo-, 2-thioxo, and 2-selenoxo-1, 3-dithiols and their analogues by phosphines and phosphites*

1.3.1.1. *Synthesis of tetrathiafulvalenes.* The trivalent derivatives of phosphorus react around 80° with 2-oxo-,[23,27,28,77–79] 2-thioxo-[26–30,36,80–82] and 2-selenoxo-[15,36,60,65,83–85] 1,3-dithiols to give the corresponding fulvalenes in various yields (5–100%) (Schemes 30–36).

This method is attractive because it allows access to a large variety of tetrathiafulvalenes bearing unsubstituted rings or rings substituted by electron-donating groups such as alkyls, cycloalkyls[65,83] or thioalkyls,[86] by electron-withdrawing groups such as nitriles,[27,28] esters,[26,85] or trifluoromethyl[29,30] or by aromatics.[36,57,78,80,83,84] The tetrathiafulvalenes are accessible in one step from the 2-thioxo-1,3-dithiols. These latter derivatives are also used as starting materials in other syntheses of tetrathiafulvalenes which require several steps from the 2-thioxo-1,3-dithiols.

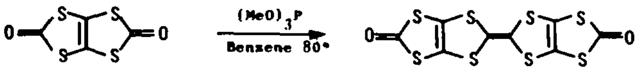
Triphenylphosphine and phosphites have been used as desulfurizing agents. The latter have been



Scheme 30.[97]

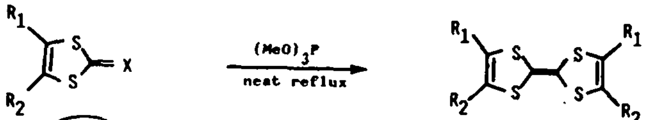
	R	Y		Yield	Ref
a	CF_3	S	$P(Ph)_3$	89	(29,30)
b	CN	O	$P(OMe)_3$	100	(27,28)
c	CN	O	$PPh_3$80°, > 24h	00	(26)
d	CN	O	$PBu_3$80°, > 24h	00	(26)
e	CN	S	"	25	(27,28)
f	CN	S	$P(Ph)_3$	5	(27,28)
g	CO_2Me	S	$P(OMe)_3$	50	(26)

Scheme 31.



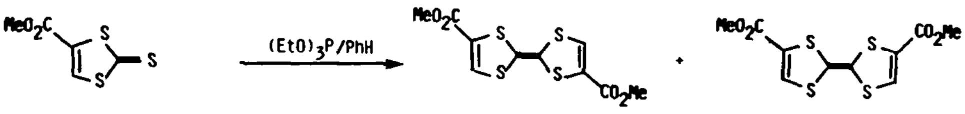
No higher homologues formed 75%

Scheme 32.[77]

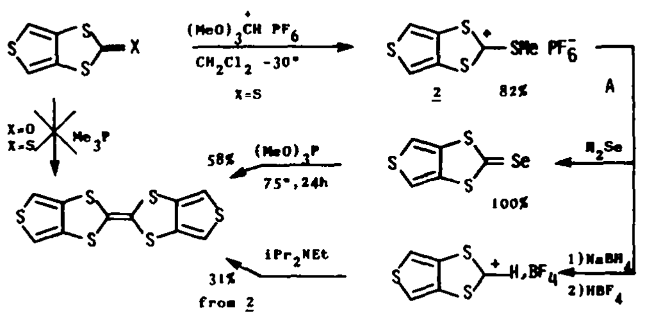


	R_1 ⌒ R_2	X	
a	S-CH=CH-S	O	No yield reported
b	$\mathrm{S{-}\underset{Me}{C}{=}\underset{Me}{C}{-}S}$	O	"
c	$S-CH_2-S-CH_2-S$	O	"
d	$S-CH_2-S$	O	"
e	$S-CH_2-CH_2-S$	S	0 %
f	$S-CH_2-CH_2-S$	O	No yield reported

Scheme 33.[23]

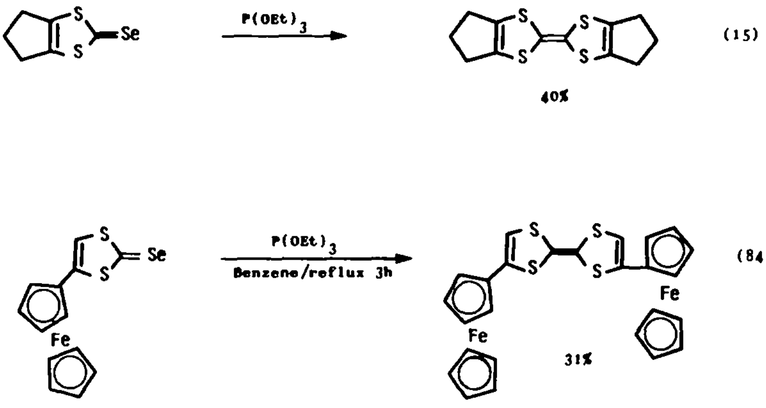


Scheme 34.[26]



route A not successful for Se or Te analogues.

Scheme 35.[60]



Scheme 36.

shown to be the most efficient.[27,28] This superiority was predictable from the work of Corey,[87] and it is surprising that the trisaminophosphines have not been used more often in difficult cases.[60]

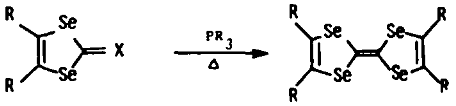
After 14 years of utilizing this method, it is unfortunate that not one systematic study has been undertaken to compare the relative merits of the 2-oxo, 2-thioxo or 2-selenoxo derivatives on the course of the reaction. Their respective advantages as a function of the nature of the substituents present on the heterocycles also remain unknown.

Thus, the oxo group seems to be superior to the thioxo group when one examines the heterocycles possessing two nitrile groups (Schemes 31(b) and (e)). The oxo group also seems to be superior to the thioxo group when the rings are substituted by sulfur groups (Schemes 33(e) and (f)). On the other hand, several other publications praise the advantage of the selenoxo derivatives[15,60,84] (Scheme 35). In this case comparative studies have been performed.[60]

Unsymmetrical 1,3-dithiolthiones (or their oxo or selenoxo analogues) react with phosphines or phosphites to give a mixture of the two possible diastereomers (Scheme 34),[26] whereas the phosphines react with mixtures of 1,3-dithiolthiones (or their oxo or selenoxo analogues)[37,39,85] to give a mixture of all possible tetrathiafulvalenes. It has been noted that the coupling by the trimethylphosphite of a mixture of 2-thioxo-1,3-benzodithiol and of 4,5-dicarbomethoxy-2-selenoxo-1,3-dithiol leads to a mixed derivative in 31%[36,85] yield, clearly superior to that resulting from the coupling with the 4,5-dicarbomethoxy-2-thioxo-1,3-dithiol (3%).[36]

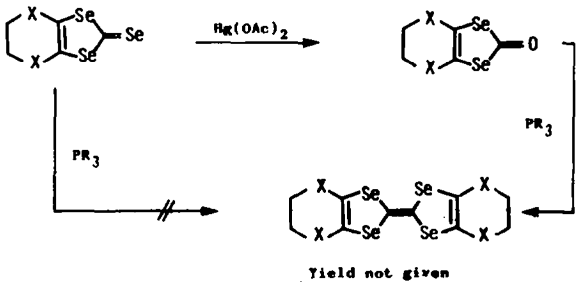
1.3.1.2. *Synthesis of tetraselenofulvalenes.* The reaction described above has been successfully applied to the synthesis of tetraselenofulvalenes, and for a long time was the only method available

(Schemes 37 and 38).[16,21,44–50,52,54,57,60,82,86,88–91] Accordingly, several 2-selenoxo-1,3-diselenols possessing hydrogens,[44,45] alkyl groups,[16,21,46–48,52,54] aryl,[21,82,88,89] or selenoalkyl groups[50,90] have been transformed into tetraselenofulvalenes by trialkylphosphites and also by triphenylphosphine. In certain cases, the advantage of employing the 2-selenoxo derivatives over the corresponding 2-thioxo derivatives has been shown (Scheme 37; compare entries 3 and 4).[21,46,47] Even so, there are some cases where the tetraselenofulvalene could not be formed from the 2-selenoxo[60] precursors and where the reaction was ineffective with the 2-selenoxo- or 2-thioxo-1,3-diselenol but gave good results with the oxygen analogue[23,90] (Scheme 38). These observations remain unexplained (see, e.g. Scheme 35).[23,60]



	R1	R2	X		Yield	Ref
1	H	H	Se	PPh$_3$ or P(OMe)$_3$, ,5h	70-80%	(44,45,58,59)
2	H	H	S	P(OMe)$_3$	0%	(58,92)
3	Me	Me	S	P(OEt)$_3$	30%	(21,52)
4	Me	Me	Se	"	86%	(46,47,52)
5	CD$_3$	CD$_3$	Se	"	90%	(47,48)
6				"	90%	(49)
7	SeMe	SeMe	Se	"	10%	(50)

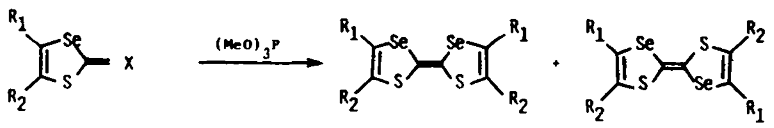
Scheme 37.



Scheme 38.[23,90]

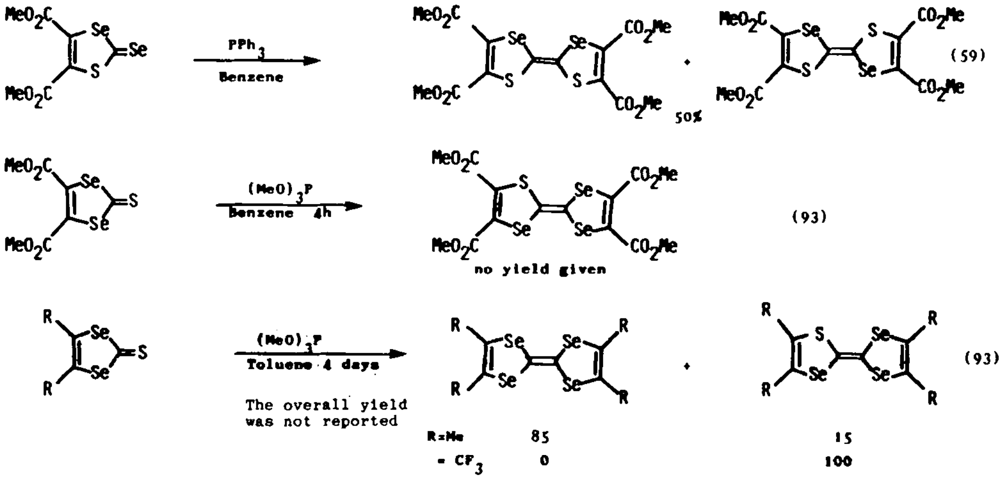
1.3.1.3. *Synthesis of diselenodithiafulvalenes.* The reaction can also be applied to the synthesis of diselenodithiafulvalenes (Scheme 39).[16,49,58,59,92] Again, the 2-selenoxo precursors are clearly superior[5,58,92] to the 2-thioxo derivatives. Certain 2-thioxo-1,3-diselenols have even produced selenotrithiafulvalenes, resulting from a rearrangement during the coupling[79,93] (Scheme 40). The mechanism of these reactions has not yet been elucidated and it is very probable that it varies as a function of the heteroatom and the substituents on the heterocycle.

Corey and co-workers[87,94–96] have shown that trialkoxy[94–96] and tris-amino phosphines[87] react with thionocarbonates and the tris-thiocarbonates. In general, this reaction gives olefins via a *syn*-elimination mechanism and it is only in the case where the decomposition of the intermediate would lead to a very strained olefin, such as *trans*-cyclohexene, or an acetylenic derivative, that the reaction follows another course and gives a tetraheterosubstituted olefin,[95,96] arising from the formal coupling of the two moieties. Corey and co-workers proposed that a 1,3-dithiaalkylidene-trialkoxyphosphorane intermediate is formed in the latter case and that it reacts via a Wittig type reaction with the starting trithiocarbonate to give the tetraalkylthiaethylenes.[95,96] This hypothesis is supported by the fact that a ketene thioacetal can be isolated when the reaction is done in the presence of benzaldehyde.[96] A different mechanism involving the formation of a thiirane intermediate was proposed by Scherowsky and Weiland[97] for the desulfurization of 1,3-benzodithiol-2-thione (Scheme

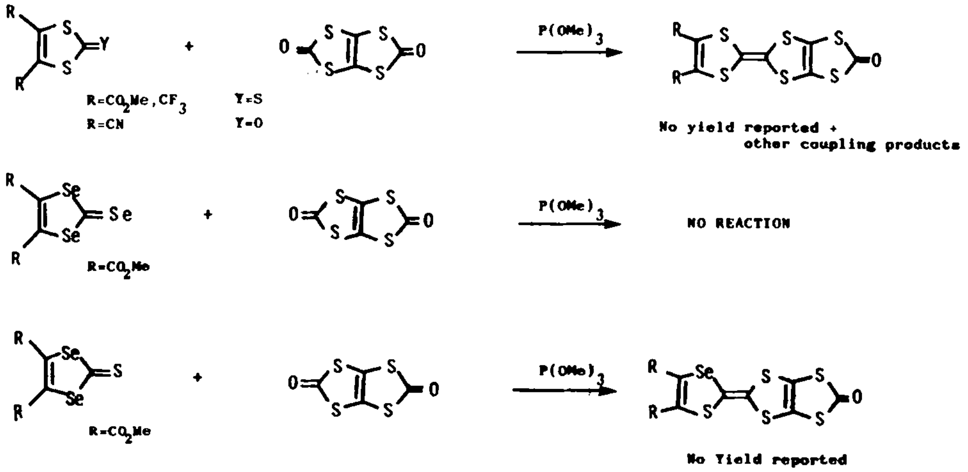


R_1	R_2	X	Yield	Ref
H	H	S	0	(58)
H	H	Se	70% ~	(58)
Me	Me	Se	60%	(92)
CH_2-CH_2-CH_2		Se	50%	(49)
CO_2Me	CO_2Me	Se	50%	(59)

Scheme 39.



Scheme 40(a).

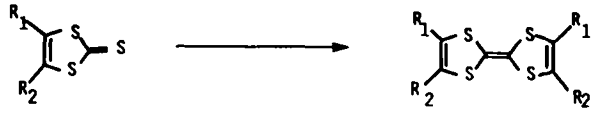


Scheme 40(b).[79]

30). But the more recent work of Miles *et al.*[28] seems to support Corey's hypothesis and extends the reaction to the case of the 2-thioxo-1,3-dithiols.

1.3.2. *Synthesis of tetrathiafulvalenes by dethiooxygenation by transition metal complexes of 2-thioxo-1,3-dithiols*

It is known that certain metal carbonyls are capable of desulfurizing trithiocarbonates and can stereoselectively form olefins[98,99] by a similar process to that which is noted in the reactions of phosphites with the same compounds. Therefore, it is reasonable to use these reactants for the synthesis of tetrathiafulvalenes starting from 2-thioxo-1,3-dithiols. The first experiments done[28] with 2-thioxo-1,3-dithiols substituted in the 3- and 4-positions by nitrile groups and iron carbonyl (Scheme 41),[12,100] led to the corresponding tetrathiafulvalene in low yields. Dicobaltoctacarbonyl proved to be more efficient (Scheme 41, entries a–c) and led to the syntheses of unsubstituted or alkyl, aryl or electron-withdrawing group substituted tetrathiafulvalenes in moderate yield (25–42%).



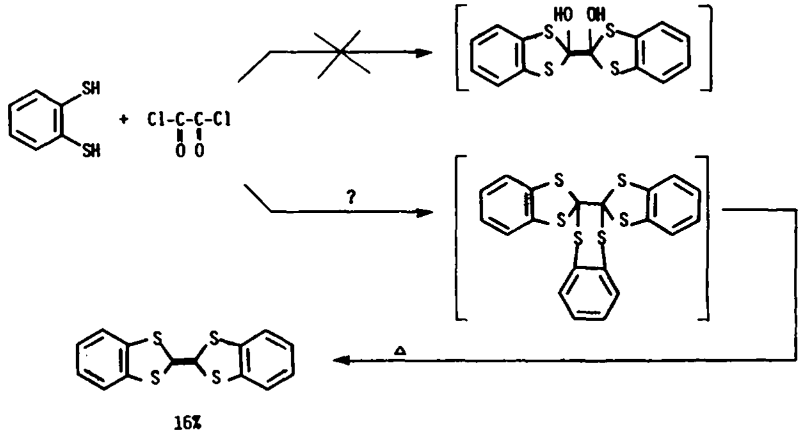
	R_1	R_2				yield	ref
a	H	H	$Co_2(CO)_8$	110°	0.5h	35%	(12)
b	Me	Me	"	80°	1h	25%	(12)
c	CH_2-CH_2-CH_2		"	110°	1h	20%	(12)
d	Ph	Ph	"	80°	2h	42%	(12)
e	CO_2Me	CO_2Me	"	80°	2h	20%	(12)
f	CN	CN	$Fe_3(CO)_{12}$			10%	(28)

Scheme 41.

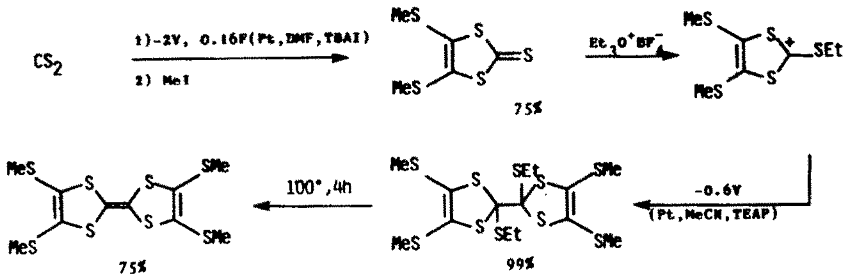
1.3.3. *Syntheses of tetrathiafulvalenes involving the elimination of two thioalkyl groups in the final step*

1.3.3.1. *β-Elimination reactions of two thioalkyl groups from hexathioorthooxalates.* Tetrathiafulvalenes are also accessible by thermal decomposition of the corresponding hexathioorthooxalates (Schemes 42–44).[17,19,24]

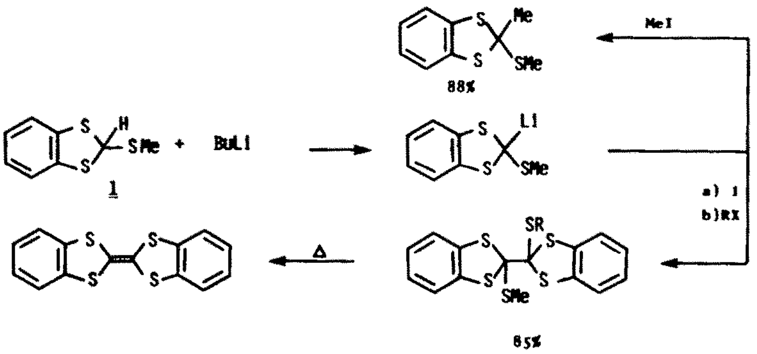
The factors favouring such a decomposition reaction have recently been studied.[19] It was noted that it is the most pure samples of hexathioorthooxalates that are the most difficult to decompose. The presence of a trace of *p*-toluenesulfonic acid or impurities arising from incomplete purification of the



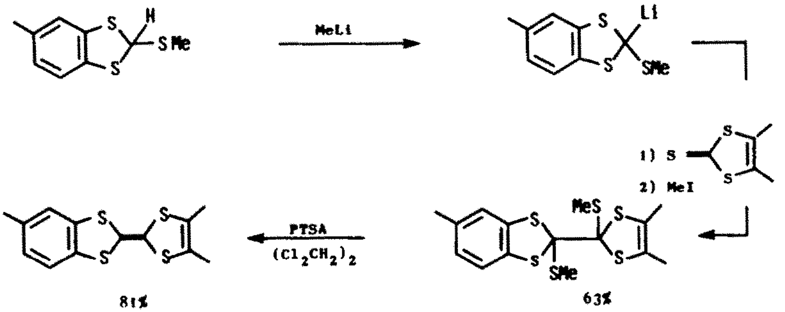
Scheme 42.[17]



Scheme 43.[24]



Scheme 44.[19,20]



Scheme 45.[19,20]

sample lowers the decomposition temperature (from 80 to 35° in CCl_4) and increases the rate of reaction.[19]

Moreover, the rate of reaction depends on the nature of the solvent.[19] For example, dibenzotetrathiafulvalene is more easily formed in 1,2-dichloroethane than in carbon tetrachloride[19,24] or toluene.[19] These observations suggest an elimination process of the two thioalkyl moieties via an ionic mechanism.[19]

This reaction can be applied not only to symmetrical hexathioorthooxalates but also to those possessing two differently substituted heterocycles (Scheme 45).[19]

These latter results are particularly interesting since they demonstrate that one can, upon having an adequate precursor (see below), obtain unsymmetrical tetrathiafulvalenes, in particular unsymmetrical benzotetrathiafulvalenes which are difficult or even impossible to prepare by another method. This is in contrast with the previously described[101,104] observations which imply a radical process during the pyrolysis of hexakis(organylthio)ethanes. In the course of this transformation the β-elimination reaction of disulfide which forms the tetrathiaethylenes is often accompanied by the homolytic rupture and reformation of the carbon–carbon bond between the two heterocycles. Such a procedure inevitably would lead to a mixture of tetrathiafulvalenes.

1.3.3.2. *Synthesis of hexathiooxalates.* One of the first syntheses of orthothiooxalate is that described by Hurtley and Smiles in 1926,[17] starting from oxalyl chloride and an excess of *o*-benzodithiol (Scheme 42).[17,103] The derivative substituted by the thiomethyl groups on the 1,3-dithiol ring has been prepared[24] by electrochemical reduction of the 2-thioethyl-1,3-dithiolium salt (Scheme 43). Finally, the reaction of 2-lithio-2-alkylthio-1,3-benzodithiols (prepared by metallation of the corresponding benzodithiol) with the 2-thioxo-1,3-dithiol, followed by alkylation of the intermediate thiolate, allows one to obtain a series of symmetrical or unsymmetrical (with respect to the central carbon–carbon bond) hexathioorthooxalates[20] (Schemes 44 and 45). These latter compounds are not easily accessible by other methods. It should be noted that the yields of tetrathiafulvalene are much higher[20] when the two entities to be coupled are substituted by aromatic rings.

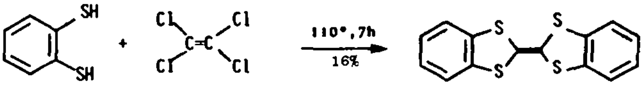
2. SYNTHESIS OF TETRAHETEROFULVALENES FROM TETRACHLOROETHYLENE

2.1. *Synthesis of tetraheterofulvalenes symmetrical with respect to the heterosubstituted carbon–carbon bond*

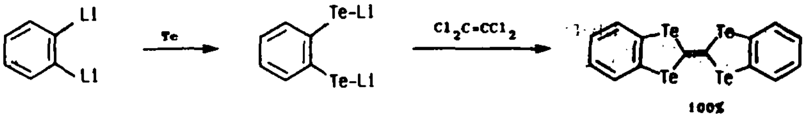
In 1926, Hurtley and Smiles[17] noted that sodium *o*-benzenedithiolate reacts with tetrachloroethylene to give the dibenzotetrafulvalene in 16% yield (Scheme 46).[17,103] In fact, this synthesis represents the first synthesis of tetrathiafulvalene ever published.

For the half century that followed, this reaction received no attention and it is only recently that a renewed interest[41,104] has been shown due to the fact that experimental conditions have been greatly improved.[104] The simplicity of the reactants proves to be a major asset of this reaction, which does not require the preliminary synthesis of heterocycles. It has found excellent application in the synthesis of several tetratellurofulvalenes,[55–57] including dibenzotetratellurofulvalenes,[55] which have been obtained in various yields (10–70%) (Schemes 47–49).

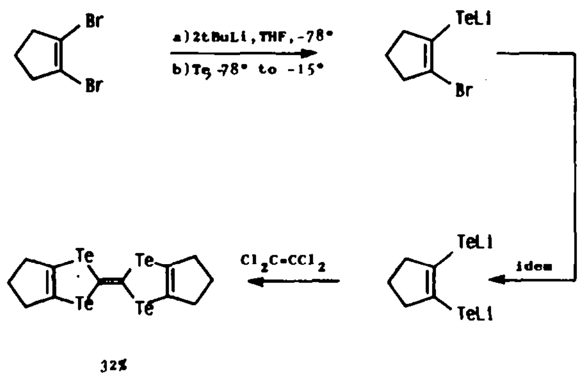
It has been noted[56] at the occasion of the synthesis of hexamethylenetetratellurofulvalene, that its selenated analogues are not accessible by the same method but a related reaction can be used to obtain[82] the dibenzotetraselenofulvalene.



Scheme 46.[17]

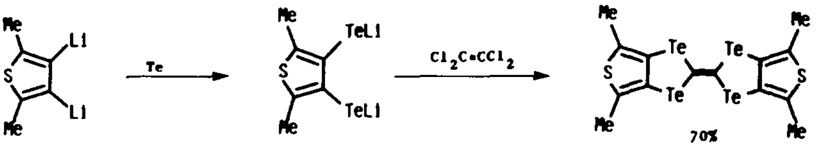


Scheme 47.[55]



Does not work for selenium analogue

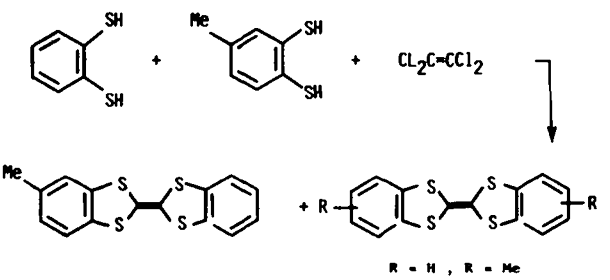
Scheme 48.[56]



Scheme 49.[57]

2.2. *Synthesis of tetraheterofulvalenes unsymmetrical with respect to the heterosubstituted carbon–carbon bond*

The method just described[104] can be used to obtain the unsymmetrical dibenzotetrathiafulvalenes (with respect to the central carbon–carbon bond) starting from tetrachloroethylene and two variously substituted *o*-benzenedithiols (Scheme 50). This synthesis is not selective and leads to a mixture of different benzotetrathiofulvalenes from which the desired derivatives can be separated.[104]



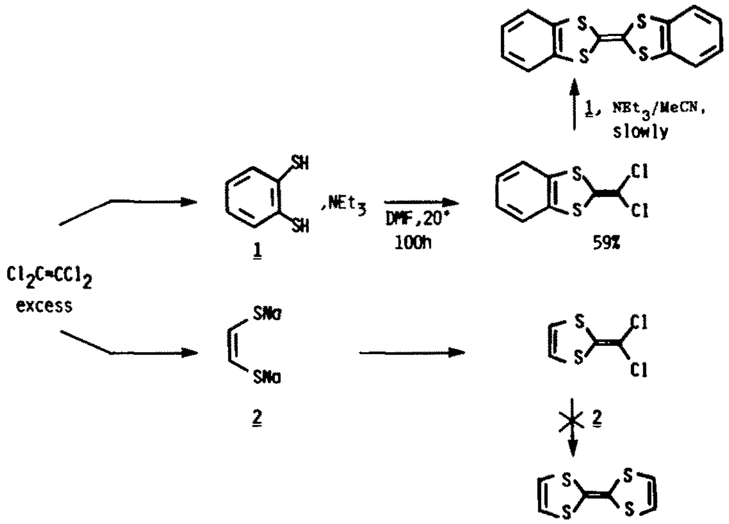
Scheme 50.[104]

Attempts at the synthesis of mixed tetrathiafulvalenes, especially monobenzotetrathiafulvalenes have not led to spectacular results,[41] but they have demonstrated the complexity of the reaction procedure. As expected this reaction is complex and probably does not involve a simple nucleophilic substitution reaction.[41,56]

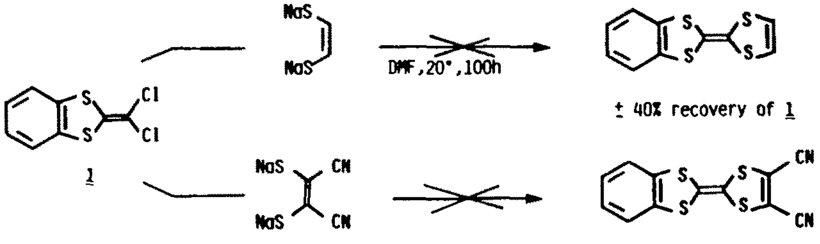
Mizuno and Cava[41] have shown that it is possible to prepare gem-dichloro derivatives by reaction of *o*-benzodithiol or sodium *cis*-ethenedithiolate with an excess of tetrachloroethylene in the presence of triethylamine (Scheme 51).

These derivatives cannot, however, be used[41] to obtain the monobenzothiafulvalenes or tetrathiafulvalenes by substitution of the two remaining halogens by sodium *cis*-dicyanoethenedithiolate or sodium *cis*-ethenedithiolate (Scheme 52).

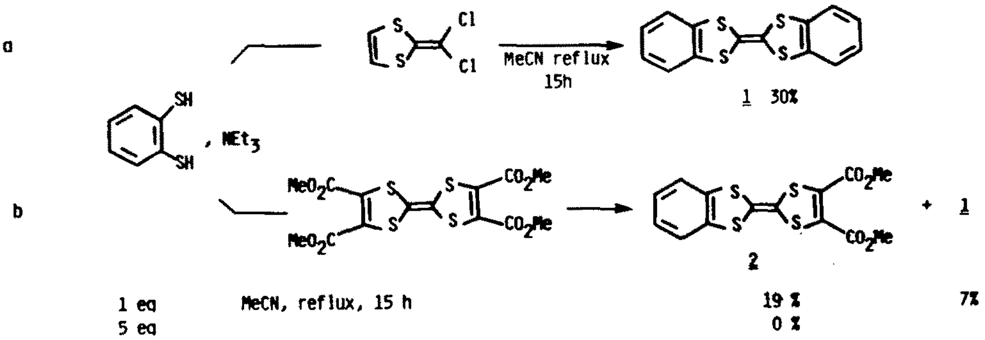
The formation[41] of dibenzotetrathiafulvalene from 2-dichloromethylene-1,3-dithiol and ammonium *o*-benzenedithiolate (Scheme 53) as well as the formation[41] of a mixture of dibenzotetrathiafulvalene and monobenzotetrathiafulvalene from tetrakis(carbomethoxy)tetrathiafulvalene and the same ammonium *o*-benzenedithiolate (Scheme 53) proves that *transdithiolation* reactions are possible during the reaction and can divert these reactions from their original course.



Scheme 51.[41]



Scheme 52.[41]



Scheme 53.[41]

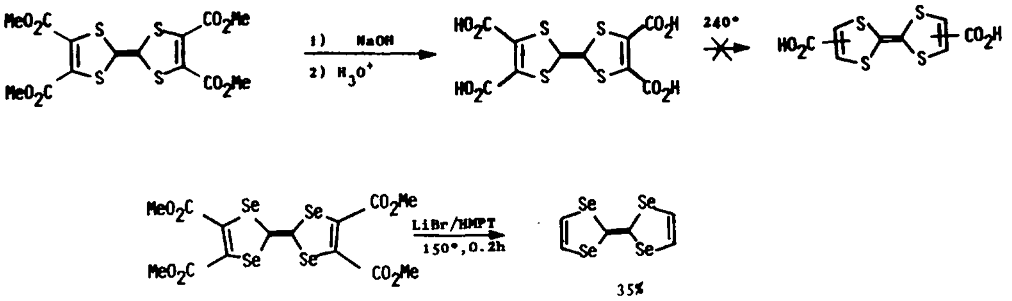
3. SYNTHESIS OF TETRAHETEROFULVALENES STARTING FROM THE GENERAL TETRAHETEROFULVALENE STRUCTURE

3.1. *Via transdithiolation*

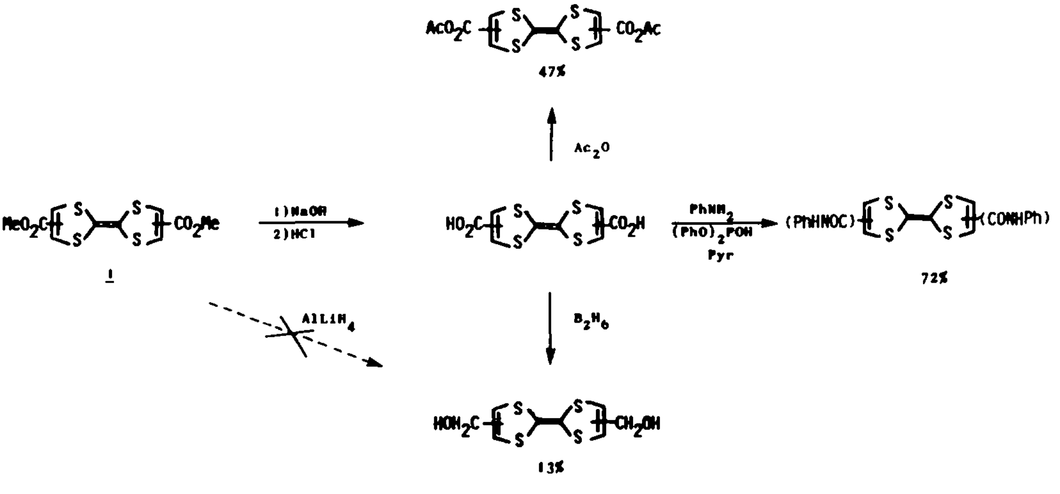
Those mentioned in the preceding paragraph and which involve a transtetra- or transdithiolation reaction starting from tetracarbomethoxytetrathiafulvalene (Scheme 53).

3.2. *Via side chain modification*

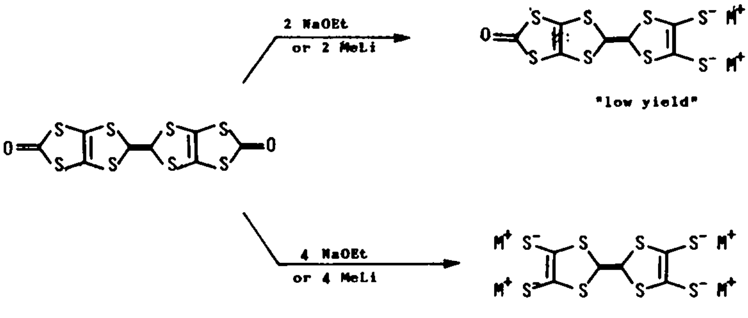
Those which result from a modification of one or several functional groups on the starting tetraheterofulvalene as shown in the following non-exhaustive selection: the hydrolysis or the decarboxylation of ester groups[26,36,53,59] (Schemes 54 and 55), the hydrolysis of the 2-thione-1,3-dithiol[77] (Scheme 56), in the formation of anhydrides,[26] esters[5,38] or amides[5,26,38] from carboxylic acids (Scheme 55).



Scheme 54.[26]



Scheme 55.[26]



Scheme 56.[77]

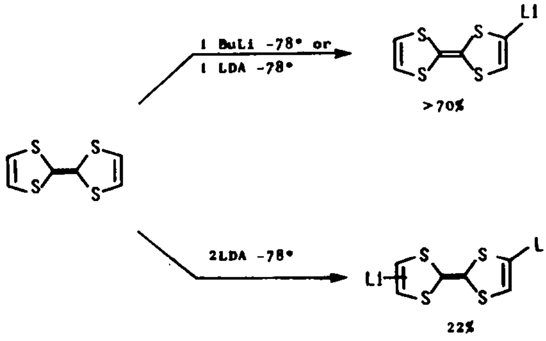
3.3. *Via metallation of tetrathiafulvalene heterocycles*

Those which involve the formation of a new carbon–carbon bond[105,106] and take advantage of the possibility of mono or polylithiation of the tetrathiafulvalene and certain homologues. Metallation of tetrathiafulvalene had been successfully accomplished at −78° by either n-BuLi or lithium diisopropylamide in ether (Scheme 57).

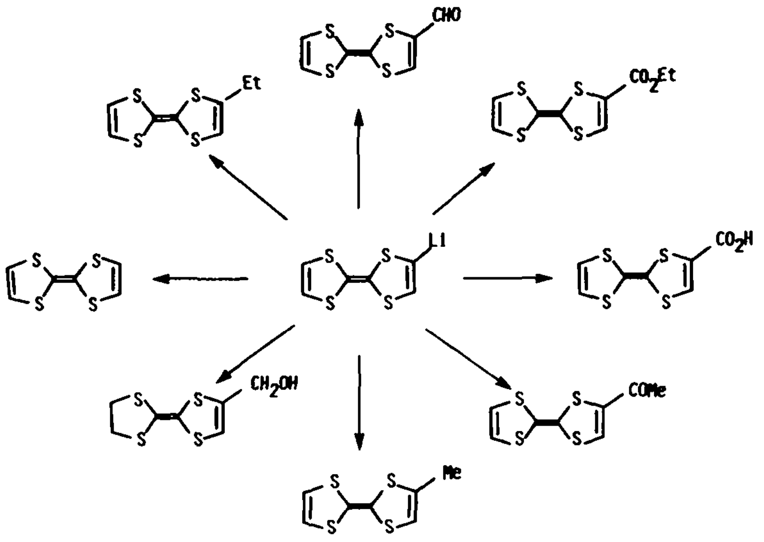
Strict temperature control is essential for the success of this reaction. In fact, around −20° a redistribution of product formation is observed which leads to polylithiated products along with tetrathiafulvalene and unidentified products.[106] 1-Lithiotetrathiafulvalene reacts at −70° with a series of electrophilic compounds to give in good yield (30–70%) the corresponding[106] carboxylic acids, esters, ketones, aldehydes or alcohols, as well as the monoalkylated tetrathiafulvalenes[106] (Scheme 58). This method affords a simple and efficient route to unsymmetrical tetrathiafulvalenes with respect to the central carbon–carbon bond.

The presence of substituents on tetrathiafulvalene exerts an important directional effect permitting control of the position of metallation. In addition, an alkyl group on the heterocycle diminishes the acidity of the adjacent proton[106] and as a consequence, favours the metallation of the other ring (Scheme 59). If each of these rings contain an alkyl group, the metallation only occurs at 25° and the anion can be trapped by ethyl chloroformate (Scheme 59). On the other hand, the presence of an ester group on one of the rings increases the acidity of the adjacent proton. Therefore, the latter is selectively attacked at −70° and gives 4,5-dicarboethoxytetrathiafulvalene via the addition of ethyl chloroformate (Scheme 59).

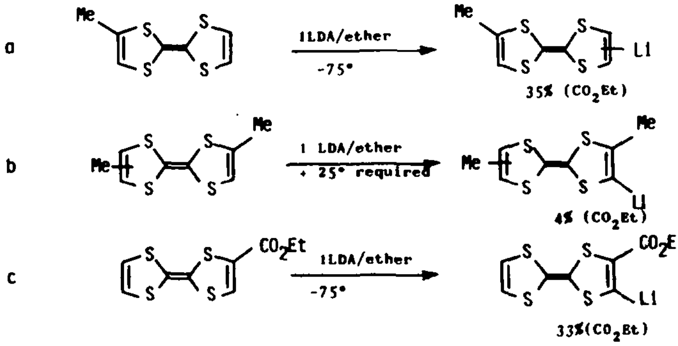
The synthesis of monofunctionalized derivatives opens the possibility to connect such tetrathiafulvalenes to other molecular systems, for example, to polymers such as chloromethylated polystyrene, which ought to give a certain mobility to the system.[106]



Scheme 57.[105,106]



Scheme 58.[105,106]



Scheme 59.[106]

4. CONCLUSION

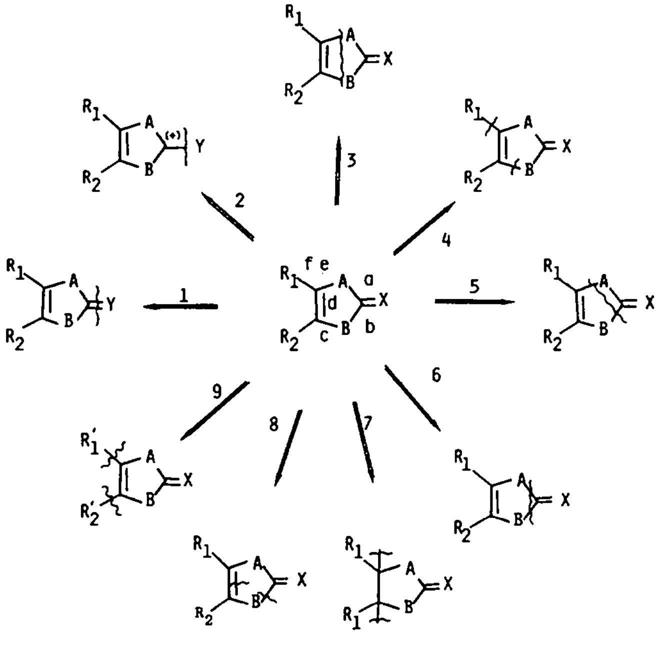
In conclusion, several efficient methods are available for the synthesis of tetraheterofulvalenes. Among these, the deoxygenation by the phosphites of 2-oxo-, 2-thioxo-, or 2-selenoxo-1,3-dithiols and their diselenated or thia-selena analogues seem to be the most versatile for the synthesis of tetrathia- and tetraselenofulvalenes. The method has not, however, been applied to tetratellurofulvalenes.

The reaction of tertiary amines with 1,3-dithiolium salts is also particularly efficient for the synthesis of tetrathiafulvalenes to the exclusion of tetraselenofulvalenes.

Finally, substitution of tetrachloroethylene by thiolates or tellurates affords tetrathiafulvalenes, tetraselenofulvalenes, or tetratellurofulvalenes. This method is actually the only one which can be used to obtain the tetratellurofulvalenes. Metallation of tetrathiafulvalenes as well as the reaction of phosphorus ylides with 1,3-dithiolium salts and 2-lithioalkylthio-1,3-dithiols with 2-thione-1,3-dithiols are particularly efficient procedures for the synthesis of tetrathiafulvalenes which are unsymmetrical about the heterosubstituted carbon–carbon double bond. The latter is most attractive for the synthesis of unsymmetrical dibenzotetrathiafulvalenes, whereas the former favours the formation of tetrathiafulvalenes substituted by carbonyl or hydroxyalkyl groups.

II. SYNTHESES OF 2-OXO-, 2-THIOXO- AND 2-SELENOXO-1,3-DIHETERO-4-CYCLOPENTENES

As was shown in Part I, the 2-oxo-, 2-thioxo-, 2-selenoxo- and 2-imino-1,3-dithioles, as well as the diselenated or thia-selena analogues, can be transformed into tetraheterofulvalenes either directly



Scheme 60.

(Section 1.2.1) or via 1,3-dithiolium salts (Section 1.1). Therefore, it is crucial to have efficient methods for the synthesis of these heterocycles.

Among the different synthetic methods available for the preparation of such compounds, there exist, on the one hand, those which involve modification of pre-existing heterocycles such as: the transformation of substituents at position 4 or 5 of the heterocycle (Scheme 60; 9) or change of the heteroatom at carbon-2 of the heterocycle (Scheme 60; 1 and 2) or, on the other hand, those which involve construction of the heterocycle (Scheme 60; 3–8). These latter methods can be classified into six general types where the heterocycle is prepared by formation of: bonds e and c (Scheme 60; 3), c and f (Scheme 60; 4), b and e (Scheme 60; 5), a and b (Scheme 60; 6), the double bond d (Scheme 60; 7) or bonds b and d (Scheme 60; 8).

At some stage of the synthesis, these reactions often involve the interconversion of the different heteroatoms at the 2-position of the heterocycle. Therefore, we will first approach the reaction type presented in Scheme 60; 1 and 2. We will then examine the different available routes to obtain the heterocyclic systems (Scheme 60; 3–8), and finally, present methods for the functionalization of side chains in the 4- and 5-positions (Scheme 60; 9).

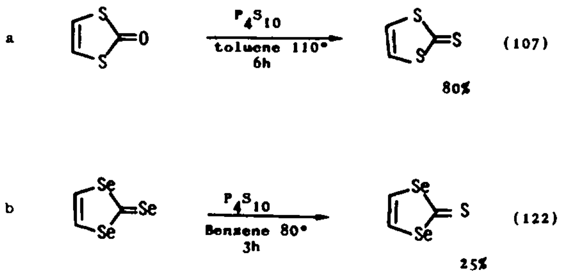
1. INTERCONVERSION OF THE 2-OXO-, 2-THIOXO-, 2-SELENOXO- AND 2-IMINO-1,3-DITHIOLS AND THEIR ANALOGUES

The 2-thioxo derivatives can be directly prepared from their oxygenated[16,107] or selenated[122] analogues by reaction with diphosphorus pentasulfide (P_4S_{10}) (Scheme 61) or with boron sulfide ((B_2S_3))[77] (Scheme 61). Reciprocally, the 2-oxo derivatives can be obtained from the thione[60,90,107] or the selones[23] using mercuric acetate[23,60,90] or mercuric oxide[107] (Scheme 62).

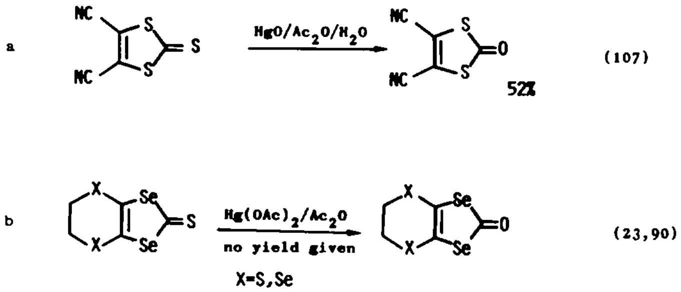
2-Thiolalkyl-1,3-dithiolium salts,[22,57,60,107] easily accessible by alkylation of the corresponding thiones (Schemes 63–65), react with primary amines[107] (Scheme 63(b)), tosyl hydrazine[22] (Scheme 64) or hydrogen selenide[60,108] (Scheme 65) to give, respectively, the 2-imino-[22,107,109] or 2-selenoxo-1,3-dithiols.[57,60]

Analogous reactions have been described starting from 2-thioxo-1,3-diseleno (Scheme 66)[57] and from 2-thioxo-1,3-selenathiol,[92,110] which allow the preparation of the corresponding 2-selones.[57,88,92,110]

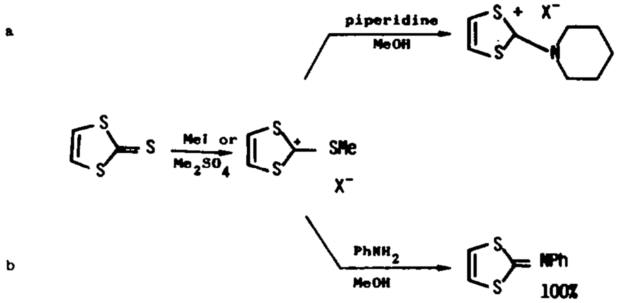
The addition of secondary amines to 2-thioalkyl-1,3-dithiolium salts leads[85,107] to 2-dialkylamino-1,3-dithiolium salts (Schemes 63(a) and 67(a)). The latter react with hydrogen selenide[108]



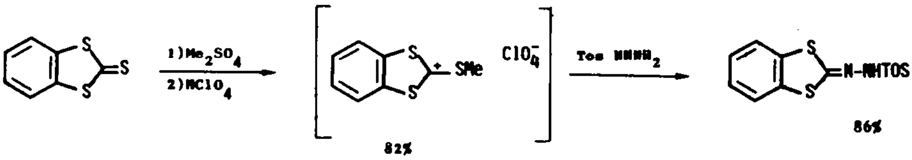
Scheme 61.



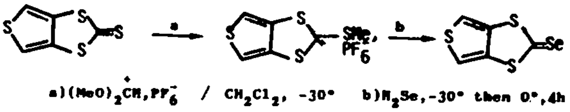
Scheme 62.



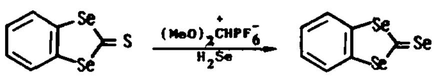
Scheme 63.[107]



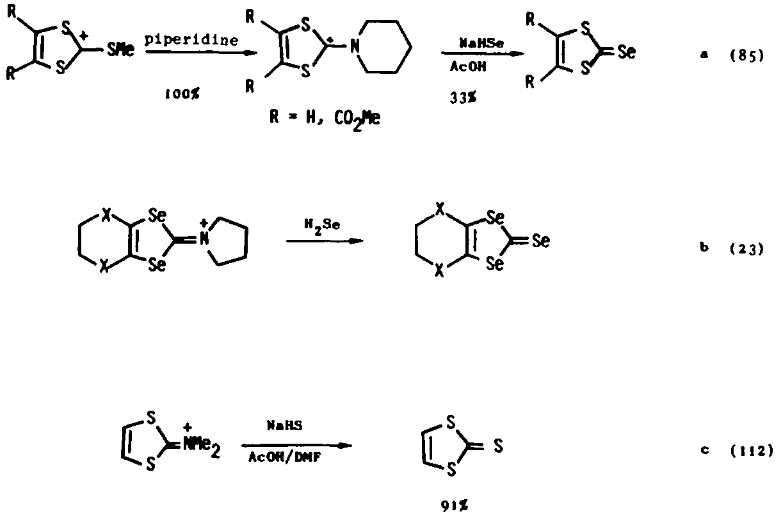
Scheme 64.[22]



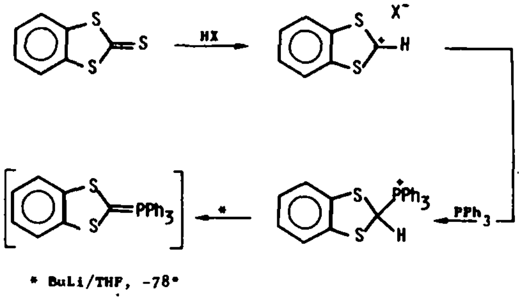
Scheme 65.[60]



Scheme 66.[88]



Scheme 67.



Scheme 68.[35]

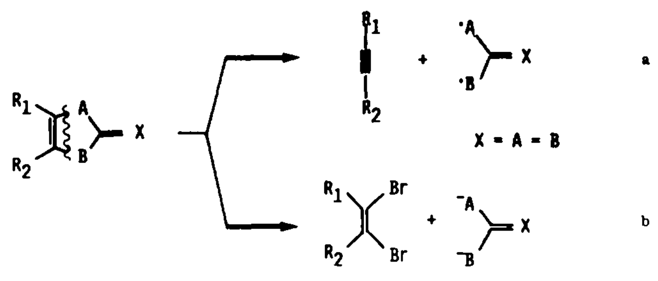
and are excellent precursors of the corresponding selones[85,111] (Schemes 67(a) and (b)). This last reaction has been successfully applied to the synthesis of 2-selenoxo-1,3-diselenols[21,23,44,46–48] (Scheme 67(b)) or of 2-selenoxo-1-seleno-3-thiols.[110] An analogous reaction affords a synthesis of 2-thioxo-1,3-dithiol[63,112] (Scheme 67(c)).

Finally, the phosphorus ylides, used by Gonella and Cava[35] in the synthesis of dibenzotetrathiafulvalenes, have been prepared[35] starting from 2-thioxo-1,3-benzodithioles, after transformation into the dithiolium salts, and successive reaction with triphenylphosphine and butyllithium (Scheme 68).

2. SYNTHESES INVOLVING CONSTRUCTION OF THE HETEROCYCLE

2.1. *Synthesis of the heterocycle by the formation of bonds e and c (Scheme 60; 3)*

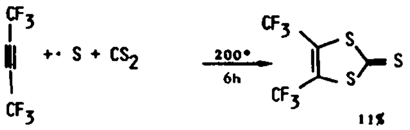
Two types of reactions are noted in this section. The first, which is by far the most widely used, involves a cycloaddition reaction of an acetylenic derivative (Scheme 69(a)), and the second uses an α,β-dihalogenated ethylene derivative (Scheme 69(b)).



Scheme 69.

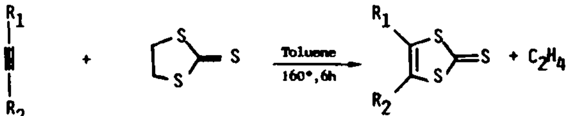
2.1.1. *Reaction of acetylenic derivatives*

2.1.1.1. *Reaction of hexafluorobutyne, sulfur and carbon disulfide.* In 1968 a group from Dupont de Nemours[113] showed that hexafluorobutyne reacts at 200° with carbon disulfide and elemental sulfur to give an 11% yield of 2-thioxo-4,5-bis(trifluoromethyl)-1,3-dithiol along with a large amount of high molecular weight material (Scheme 70).



Scheme 70.[113]

2.1.1.2. *Exchange reaction between acetylenic compounds and ethylene trithiocarbonate derivatives and related compounds.* The same heterocycle can be obtained in much higher yield by reaction of the same hexafluorobutyne and ethylene trithiocarbonate[114] (Scheme 71(b)).

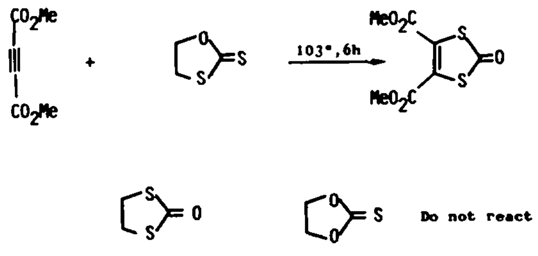


	R_1	R_2	Yield	Ref
a	CO_2Me	CO_2Me	76	(115)
b	CF_3	CF_3	76	(114)
c	H	CN	33	(114)
d	H	H	6	(114)

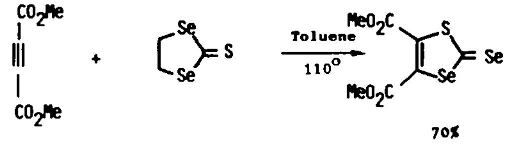
Scheme 71.

This type of reaction was first reported by Easton and Leaver[115] in which they reacted the same trithiocarbonate and dicarbomethoxyacetylene. It is particularly efficient when the acetylene derivative contains electron-withdrawing groups (CF_3, CO_2R, CN)[11,26,114,115] (Scheme 71). Acetylene itself requires much more rigorous conditions and gives a token yield[114] of 1,3-dithiol-2-thione, while 1-phenyl 1-propyne and diphenyl acetylene do not react[114] under the usual conditions (140°) and give only tars at higher temperatures (190°).[114] The reaction is not limited to trithiocarbonate and the presence of a phenyl group on the heterocycle seems to favour the formation of the 1,3-dithiol-2-thione.[114]

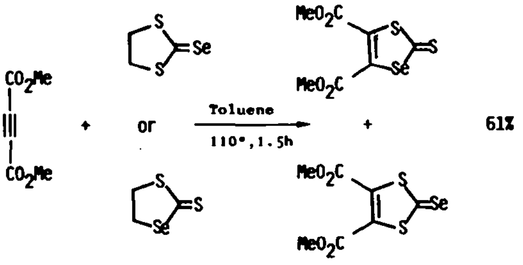
This process has been extended with moderate success to the synthesis of analogues bearing other heteroatoms. Moreover, it has been shown that, using dicarbomethoxyacetylene as a model, there is no reaction with S,S′-ethylenedithiocarbonate[114] and the O,O′-ethylenethiocarbonate under various reaction conditions (60°, 110°, or 160°) (Scheme 72). If the saturated heterocycle used in the reaction with dicarbomethoxyacetylene contains different heteroatoms, it leads to the formation of unsaturated heterocycles which, in general, do not retain the heteroatoms originally present in the heterocyclic starting material. Thus, O,S-ethylenedithiocarbonate[116] and Se,Se-ethylenethiocarbonate,[59] form respectively, the 2-oxo-1,3-dithiol[114] (Scheme 72) and 2-selenoxo-1,3-selenathiol[59] (Scheme 73). S,Se-Ethylenethiocarbonate[85] and its S,S-ethyleneselenocarbonate[85] isomer react under similar conditions but both give the same mixture of 2-selenoxo-1,3-dithiol and 2-thioxo-1,3-selenathiol (Scheme 74). A mechanism rationalizing the different observations has been proposed.[85,117]



Scheme 72.[114]

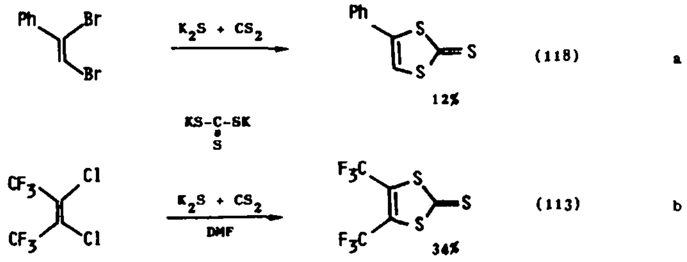


Scheme 73.[59,85]



Scheme 74.[85]

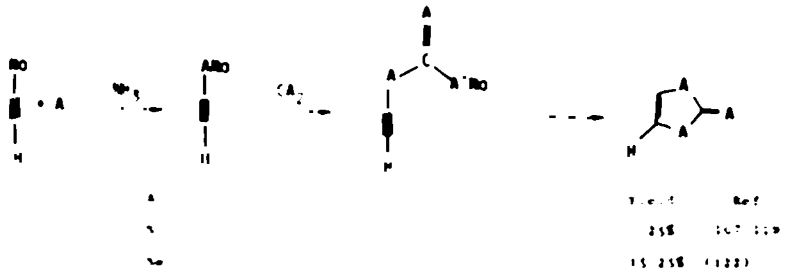
2.1.1.3. *Reaction of potassium trithiocarbonate with β-dihalogenoethylenes.* The reaction of potassium trithiocarbonate, prepared from potassium sulfide and carbon disulfide, with 2,3-dichloro-2-hexafluorobutene[113] and 1,2-dibromostyrene[118] gives 2-thioxo-1,3-dithiols from readily available starting materials but in only average yields (Scheme 75) (compare Scheme 75(b) to Schemes 70 and 71(b)).



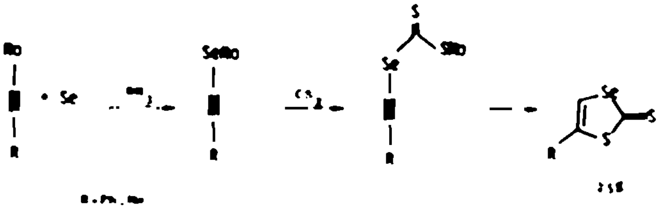
Scheme 75.

2.2. *Synthesis of the heterocycle by formation of bonds c and f (Scheme 60; 4)*

In 1964, Mayer and Gebhardt[107,119] described the preparation of 2-thioxo-1,3-dithiol from sodium acetylide, elemental sulfur and carbon disulfide (Scheme 76). This reaction has been applied[120] to the synthesis of 2-selenoxo-1,3-diselenol by using selenium and carbon diselenide.[121] This approach was later extended to the preparation of 5-phenyl-2-thioxo-1,3-selenathiol[120] and of 5-methyl-2-thioxo-1,3-selenathiol[122] from the corresponding acetylene, selenium and carbon disulfide (Scheme 77).



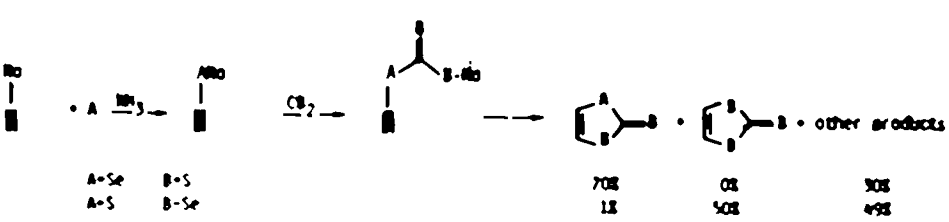
Scheme 76



Scheme 77[120,122]

Treatment[58,122] of sodium acetylide with selenium and carbon disulfide or with sulfur and carbon diselenide does not give exclusively the expected product on the basis of previous experience, but a mixture of five or six heterocycles of which the majority are shown in Scheme 78. These observations have been rationalized.[122]

Even if the syntheses presented in this section have the advantage of being expedient, they lead to heterocycles in very modest yields. Moreover, no effort seems to have been made to adapt the method to the syntheses of heterocycles disubstituted in positions 4 and 5.

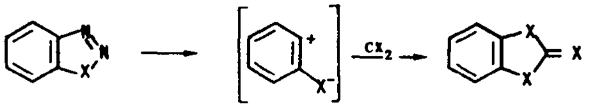


Scheme 78[123]

2.3. *Synthesis of the heterocycle by formation of bonds e and b* (*Scheme* 60; 5)

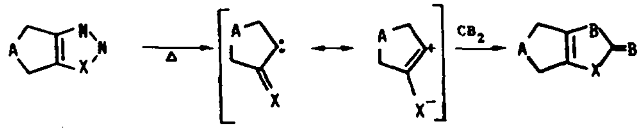
This approach takes advantage of the formation of 1,3-dipoles during the thermolysis (150–220°) of 1,2,3-thiadiazoles^{68,123,124} and of 1,2,3-selenadiazoles.^{16,54,89,125} These can be trapped by carbon disulfide which is used as a solvent, or by carbon diselenide^{121} (2 equiv) in xylene, which gives the corresponding heterocycles.^{16,54,68,89,110,123,124a,125} This reaction can be used to obtain, among other things, in good yield, 2-thioxo-1,3-benzodithiol^{123,124a} and its selenated analogue^{89} (Scheme 79), 4,5-cycloalkyl-2-thioxo-1,3-dithiol^{68} and 2-thioxo-1,3-selenathiol (Scheme 80).^{16,110}

The method does not apply to the synthesis of 2-thioxo-1,3-dithiol.^{110} This failure has been attributed^{110} to fragmentation of the 1,3-dipole into acetylene and sulfur; such a process is much less favourable if the decomposition of the dipole leads to a strained cycloalkyne such as benzyne^{89,123,124a} or cyclopentyne.^{68,110} The dipole is then involved in a cycloaddition reaction (Schemes 79 and 80).



	Yield	Ref
X=S	84%	(123,124a)
X=Se	69%	(89)

Scheme 79.



X	A	B		Yield	ref
S	CH₂	S	215°, 7h	43%	(68)
Se	CH₂	S	160°	54%	(110)
Se	S	Se	110°, 2h	35%	(54)

Scheme 80.

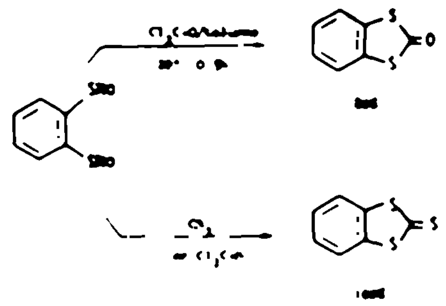
2.3.1. *Related reactions*

The reaction of benzyne, generated by the pyrolysis of phthalic anhydride at 100°, with carbon disulfide,^{74} gives 1% of 1,3-benzodithiol-2-thione and can be formally related to the reactions previously mentioned in this section.

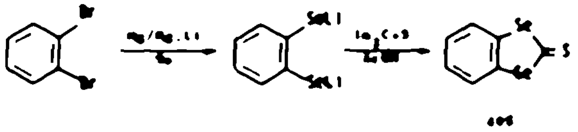
2.4. *Synthesis of the heterocycle by formation of bonds a and b* (*Scheme* 60; 6)

This strategy involves the reaction of an ethylene dithiolate or its diselenated analogue with phosgene, thiophosgene, carbon disulfide or a related derivative such as carbonyl or thiocarbonyldiimidazole. It becomes particularly attractive when the organometallic compound is available. Effectively, it is the case of sodium *o*-benzenedithiolate generated^{148} by the action of sodium hydroxide with commercial *o*-benzenedithiol (Scheme 81) and of its selenated analogue, lithium *o*-benzenediselenolate^{88} generated from the *o*-dilithiobenzene,^{126,127} and selenium (Scheme 82). It is also the case of the sodium salt of dimercapto maleonitrile prepared^{122} in excellent yield by the action of sodium cyanide on carbon disulfide (Scheme 83). Alternatively, the same compound can be prepared^{107} by the action of hydroxide with 4,5-dicyano-2-thioxo-1,3-dithiol dissolved in ethanol. Such a type of reaction is applicable to other 2-oxo- and 2-thioxo-1,3-dithiols, including^{107} 2-oxo-1,3-dithiol.

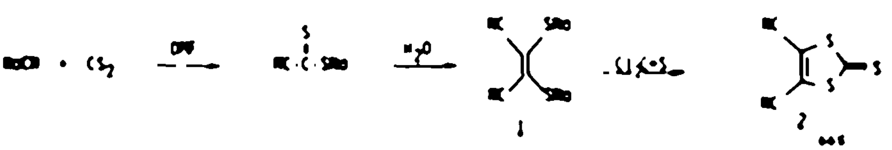
Among other things, this method allows the synthesis of 2-oxo- and 2-thioxo-1,3-benzodithiol (Scheme 81), and of 2-thioxo-1,3-benzodiselenol,^{88} starting from *o*-dibromobenzene (Scheme 82), as



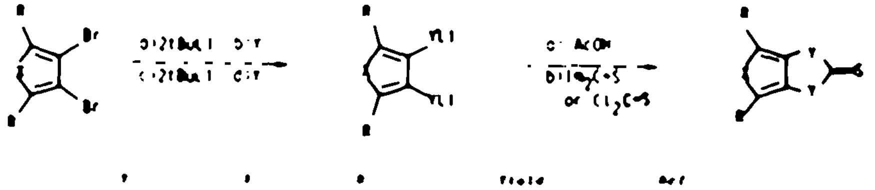
Scheme 81[148]



Scheme 82[88]



Scheme 83[96,107,128]



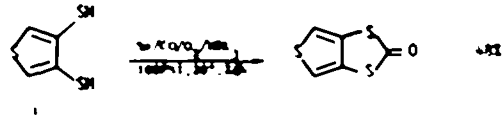
Y	X	R	Yield	Ref
S	S	H	33*	(181)
S	S	Me	30	(157)
S	Se	H	17*	(181)
Se	S	H	30	(160)
Se	S	Me	10	(157)
Te	S	H	14 (impure)	(160)

* no reaction if CS_2 is used instead

Scheme 84

well as of 4,5-dicyano-2-thioxo-1,3-dithiole[96,107] from potassium cyanide and carbon disulfide[96] (Scheme 83) in appreciable yields. It was successfully applied to the synthesis of 1,3-dithiolo[4,5c]thiophene-2-thione, of 1,3-diselenolo[4,5c]thiophene-2-thione and of 1,3-dithiolo-[4,5c]selenophene-2-thione. For the most part, these derivatives have been coupled to the related tetraheterofulvalenes (Scheme 84).

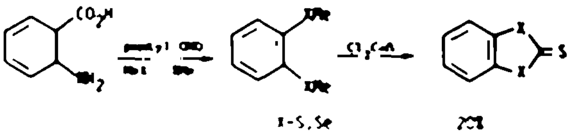
1,3-Dithiolo[4,5c]thiophene has also been successfully synthesized[60] by carboxylation of the β-dithiol 1 in the presence of selenium and triethylamine (Scheme 85), according to a recently described procedure.[129]



Scheme 85[90]

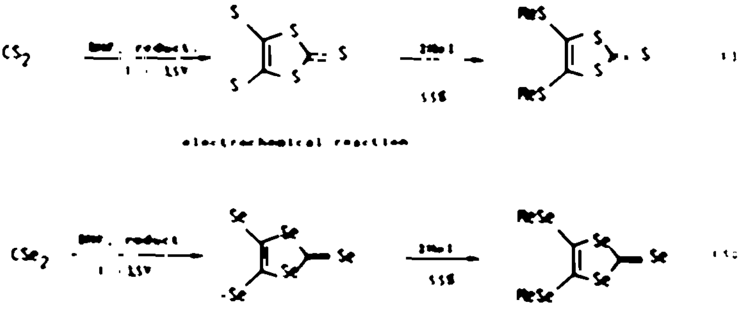
2.4.1. *Related reactions*

2.4.1.1. *Syntheses involving phosgene and methylthiobenzene heterosubstituted in the* ortho *position.* 2-Thioxo-1,3-benzodiselenol, its sulfur analogue in the 1-position and 2-thioxo-1,3-benzodithiol have been prepared[82] in modest yield by action of thiophosgene at −80° with, respectively, *o*-di(methylthio)benzene, 1-methylseleno-2-methylthiobenzene or *o*-di(methylthio)benzene (Scheme 86). These last products have been generated by the action of benzyne with dimethyl diselenide, methyl selenomethyl sulfide and dimethyl disulfide, respectively. Unfortunately, the method is not applicable to the synthesis of 2-thioxo-1,3-benzoditellurol.[82]



Scheme 86[82]

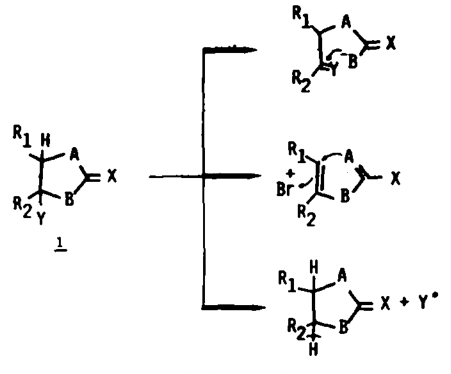
2.4.1.2. *Syntheses involving electrochemical reduction of carbon disulfide and carbon diselenide.* The strategy described in this section can also be related to the syntheses of 4,5-di(alkylthio)-2-thioxo-1,3-dithiol[130,131] and its selenated analogue[50,90] which involve, respectively, the electrochemical reduction of carbon disulfide and carbon diselenide (Scheme 87). In the latter case, it was noted[90] that minor variations in temperature play an important role in the yield of the reaction.



Scheme 87

2.5. *Synthesis of the heterocycle by formation of bond d in the last step of the reaction*

This double bond can be formed by a β-elimination reaction involving the departure of a proton and a heteroatom in positions 4 and 5 of the pre-existing heterocycle 1 (Scheme 88). In general, the elimination of these two groups occurs easily due to the stabilization of the intermediate carbenium ion by the heteroatom contained in the ring. Therefore, the construction of the heterocyclic structure bearing the leaving groups in position 4 or 5 becomes the major problem. Scheme 88 shows some of the different possible routes to such a precursor.

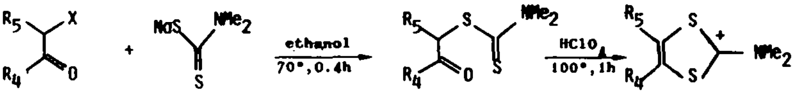


Scheme 88.

2.5.1. *Synthesis of the heterocycle by formation of bonds c and d (Scheme 60; 8)*

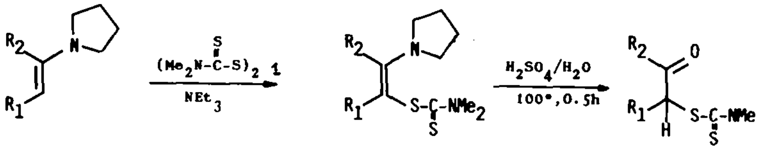
2.5.1.1. *Synthesis of salts of 2-N,N-dialkylamino-1,3-dihetero-4-cyclopentene. Reactions involving the cyclization of a β-oxo-dithiocarbamate: syntheses of 2-N,N-dialkylamino-1,3-diselenolium and N,N-dialkylamino-1,3-selenothiolium salts.*

(1) β-Oxo-N,N-dialkylthiocarbamates are easily cyclized by sulfuric or perchloric acid to 2-N,N-dialkylamino-1,3-dithiolium salts[15,16,63,65,84,112,132–134] possessing in positions 3 and 4 either two hydrogens,[112] or one or two alkyl,[63,72,133] cycloalkyl,[16,65,71,72] or aryl[84,133] groups (Schemes 89 and 90). These have been proven to be excellent precursors for 2-thioxo-1,3-dithiols[15,63,65,71,72,84] and of 2-selenoxo-1,3-dithiols,[15,16,65,84] when they are treated with, respectively, hydrogen sulfide or hydrogen selenide.†[135] The β-oxo-N,N-dialkylthiocarbamates are readily available[15,16,63,65,84,132]



R_4	R_5	Yield %	Yield %	Ref
Me	H	81	44	(55)
Me	Me	95	45	(55)
Ph	H	95	95	(55)
$pMeC_6H_4$	H	86	79	(55)
$pNO_2C_6H_4$	H	94	82	(55)
ferocenyl	H	—	63	(84)
$CH_2-CH_2-CH_2$		—	100	(51)

Scheme 89(a).



R_1	R_2	Yield	Yield
Ph	Ph	94 %	95 %
$CH_2-CH_2-CH_2-CH_2$		–	87 %
$CH_2-CH_2-CH_2$		–	88 %
H	Ph	–	65 %
Ph	H	–	42 %

Scheme 89(b).[51]

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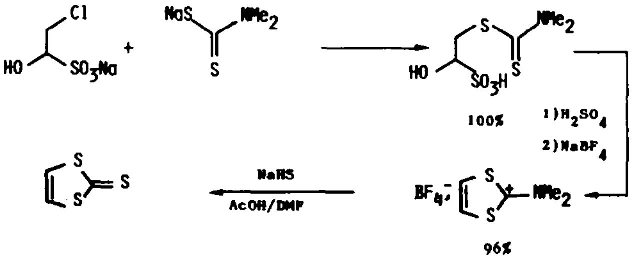
† Available *inter alia* from Matheson Gas Products, P.O. Box 85, East Rutherford, NJ 07073, U.S.A., or prepared from Al_2Se_3. See Ref. 135.

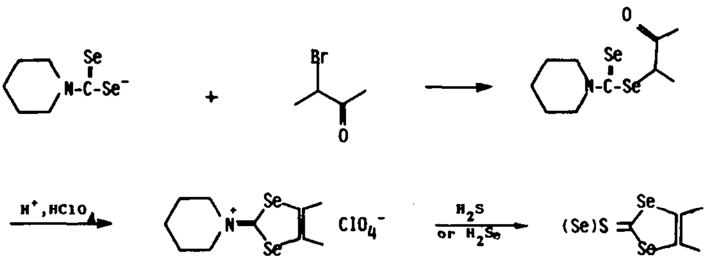
from α-halogenoketones and sodium dialkylammonium N,N-dialkylaminodithiocarbamates,[136] or by the action of enamines[51] with the disulfide 1 (Scheme 89).

The reaction of sodium dithiocarbamate with chloroacetaldehyde does not lead to the expected product,[112] and the substitution is not even effective[112] with 2-bromo-1,1-diethoxyethane. 2-N,N-Diethylamino-1,3-dithiolium salts possessing hydrogens on carbons 4 and 5, on the other hand, can be prepared[112] from sodium dithiocarbamate and 2-chloro-1-hydroxy-1-sulfonatoethane via cyclization in acidic media (Scheme 90).

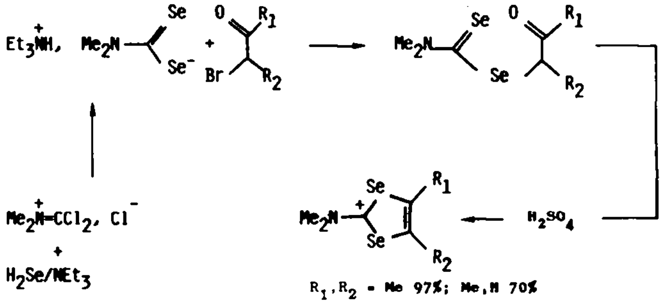


Scheme 90.[112]

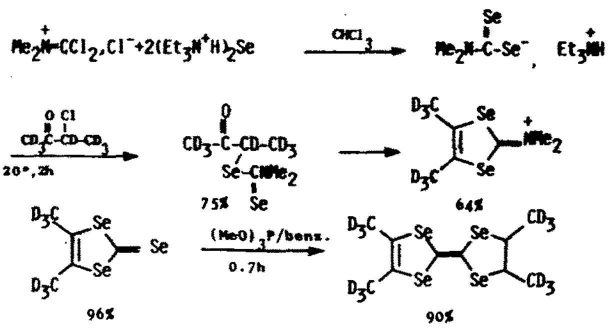
(2) 2-N,N-Dialkylamino-1,3-diselenolium salts have been successfully prepared from α-halogenoketones by a series of reactions similar to that described in the preceding section for 1,3-dithiolium salts (Schemes 91–96). This involves the utilization of tetraalkylselenourea[49,137,138] (Scheme 95) for the N,N-dialkylaminoselenocarbamato salts[16,21,23,27,46–48,111] for which the preparation[139,140] requires the use[16,21,27] of carbon diselenide,[21] which is not easily available and is malodorous. Recently, many more efficient syntheses of diselenocarbamate, which do not utilize



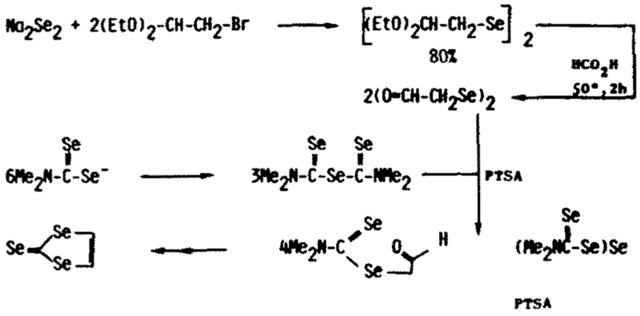
Scheme 91.[21,27]



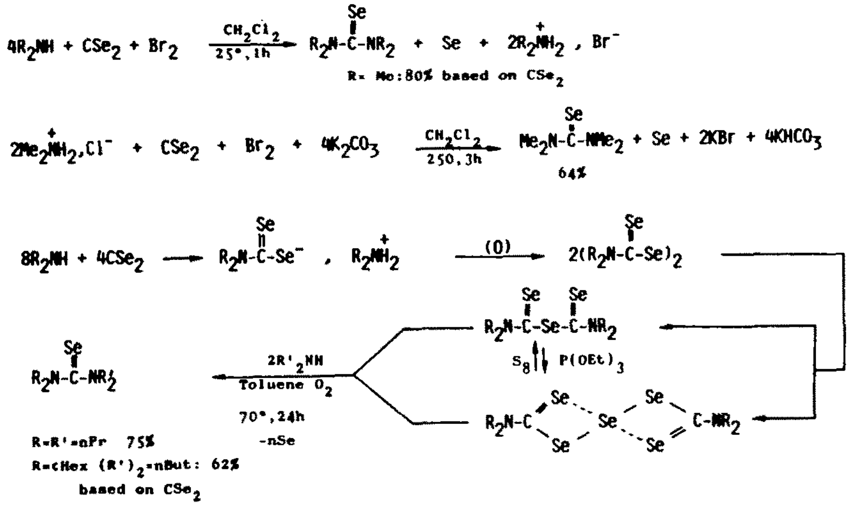
Scheme 92.[47]



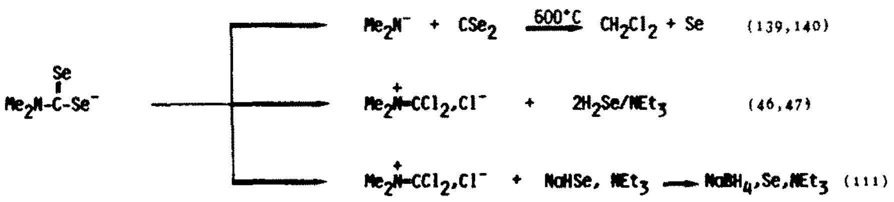
Scheme 93.[47,48]



Scheme 94.[44]



Scheme 95.[137,138]



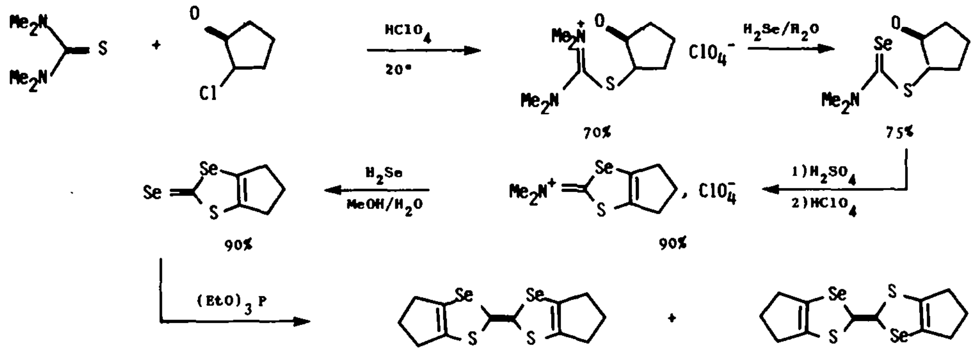
Scheme 96.

carbon diselenide, have been published. These methods employ dichloromethylene(dimethyl)-ammonium salts[141] which are commercially available products,[142] triethylamine and hydrogen selenide[46,48] or, even better, sodium hydrogen selenide (NaHSe)[111] generated in DMF by action of sodium borohydride on elemental selenium (Schemes 95 and 96).

These reactions provide a synthesis of 2-N,N-dialkylamino-1,3-diselenolium salts containing alkyl,[27,46,47,49,111,132,143] deuteromethyl,[48] cycloalkyl,[46,143] thioalkyl,[16,23] selenoalkyl[23] and aryl[21,143] groups at position 4 or 5 (Schemes 91–94). The latter derivatives have been employed in the synthesis of 2-thioxo-1,3-diselenols,[21,27,111,143] 2-selenoxo-1,3-diselenols[21,23,44,46–48,111,143] and 2-oxo-1,3-diselenols[23] (Schemes 91–94).

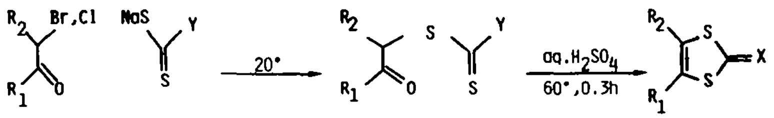
The 2-halogenoaldehydes and their acetals do not react[44] with the salts of diselenocarbamate. However, aldehydes containing an (N,N-dialkyldiseleno)carbamato group in the *β*-position are available by hydrolysis of the corresponding acetals.[44] These are prepared by an exchange[137–139] reaction between a diselenide functionalized in the *β* and *β'* positions and an N,N-dialkyldiselenocarbamoyl selenide (Scheme 94). This reaction can be used to prepare 2-selenoxo-1,3-diselenol with a hydrogen at positions 3 and 4 (Scheme 94).

(3) Syntheses of 2-N,N-dialkylamino-1,3-selenothiolium salts[49] involve modification of the method cited in the preceding section. 2-Chlorocyclopentanone is treated with tetramethylthiourea to give the corresponding thiouronium salt. This is transformed[49] into the thioselenocarbamate then into the 2-N,N-dialkylamino-1,3-selenathiolium salt by successive action of hydrogen selenide and a mineral acid (Scheme 97).



Scheme 97.[49]

2.5.1.2. *Syntheses involving β-keto methyltrithiocarbonates or β-keto-o-alkylthiocarbonates in acidic media.* 2-Thioxo-[134] and 2-oxo-1,3-dithiols[16,77,134,144,145] have also been prepared by cyclization in acidic media, respectively from *β*-keto-methyltrithiocarbonates,[134] or from *β*-keto-*o*-isopropyl[16,77,144,145] or *o*-ethyl-[134,145] dithiocarbonates. These compounds are easily accessible from *α*-halogenated ketones and sodium methyltrithiocarbonate[70] or from potassium *o*-isopropyl (or *o*-ethyl) xanthate[13] (Scheme 98).



Y	R_1	R_2	Yield	X	Yield	Ref
OiPr	Ph	H	90	O	92	(145)
	$pNO_2C_6H_4$	H	90	O	90	"
	$pCF_3C_6H_4$	H	92	O	60	"
	Me	H	81	O	63	"
	Ph	Ph	80	O	85	"
	Me	Et		O	65	"
	CH_2 — $(CH_2)_2$ —	CH_2	81	O	85	"
OEt	$pNO_2C_6H_4$	H		O	73	(134)
	$pClC_6H_4$	H		O	0	"
SMe	Ph	H		S	93	"
	$pNO_2C_6H_4$	H		S	75	"
	OH	H		S	31	"

Scheme 98.

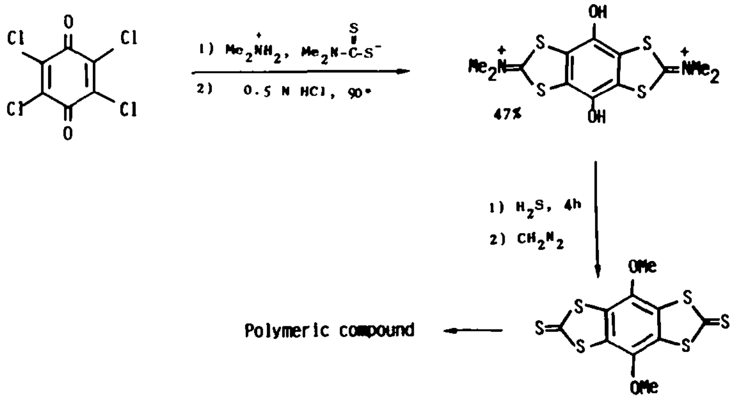
2.5.1.3. *Related reactions.* These involve:

(1) The synthesis of N,N-dialkylamino-1,3-benzodithiolium salts from dimethylammonium dimethyldithiocarbamate and 2,3-dichloronaphthoquinone, chloranil or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. This transformation very likely[69] involves an addition–elimination to the quinone system (Scheme 99).

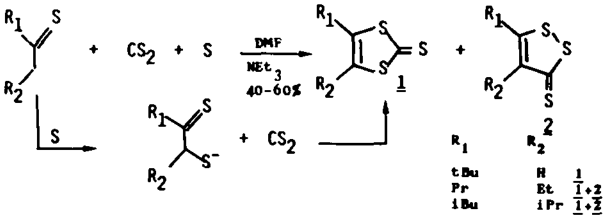
(2) The reaction[146] of thiones with carbon disulfide in the presence of sulfur (Scheme 100).

(3) The formation of the bromide of 2-N,N-dimethylamino-1,3-dithiol (Scheme 101) obtained[147] by the thermal dehydrobromination of the heterocycle resulting from the bromination of S-vinylthiocarbamate.

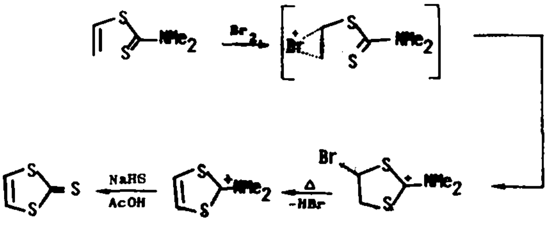
(4) The formation[107] of 2-oxo-1,3-dithiol by the bromination–dehydrobromination reaction of 2-oxo-3,4-dihydro-1,3-dithiol (Scheme 102).



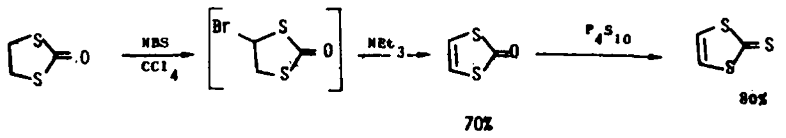
Scheme 99.[69]



Scheme 100.[146]



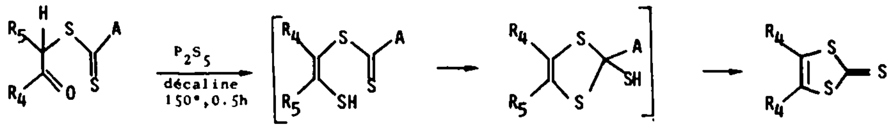
Scheme 101.[147]



Scheme 102.[107]

2.6. *Synthesis of the heterocycle by formation of bonds d and b (Scheme 60; 8)*

β-Oxoalkyltrithiocarbonates[70] and β-oxo-*o*-alkyldithiocarbonates[13,16,70,71] react around 140° with diphosphorus pentasulfide to give the 2-thioxo-1,3-dithiols (Scheme 103).



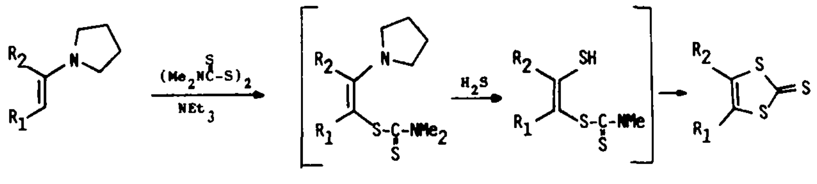
A	R_4	R_5	Yield	Ref
SMe	Ph	H	35	(70)
OEt	Ph	H	35	"
	Me	H	23	"
	H	H	8	"
	Me	Me	72	(13)
	Me	Et	35	"
	CH_2 — CH_2 — CH_2		15	"

Scheme 103.

This method for the synthesis of the heterocycle does not seem to offer any substantial advantage over that already cited (Section 2.5.1.2) which, starting with the same substrates, involves their cyclization in acidic media by successive formation of bonds c and d.

2.6.1. *Related reactions*

Alternatively, the 2-thioxo-1,3-dithiols can be prepared[51] by reaction of hydrogen sulfide with enamines containing an N,N-dimethylaminodithiocarbamato group on the β-vinyl carbon (Scheme 104). These latter compounds are accessible via the corresponding enamine (Scheme 104).



R_1	R_2	Yield
Ph	Ph	98
CH_2-CH_2-CH_2-CH_2		69
CH_2-CH_2	CH_2	32
Ph	H	62
CH_2CO_2Et	H	37

Scheme 104.[51]

2.7. *Functional group modification of substituents on carbons 4 and 5 of the pre-existing heterocycle (Scheme 60; 9)*

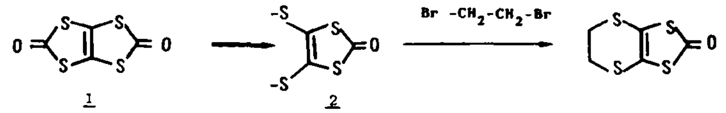
At the beginning of this section, methods have already been presented which allow one to replace the heteroatom bonded at C-2 of the heterocycle. In summary, presented in this section, are reactions which allow modifications of the side chains of the heterocycle. These reactions permit access to compounds which are often difficult to obtain by other methods.

Among the examples described in the literature, the following were selected:

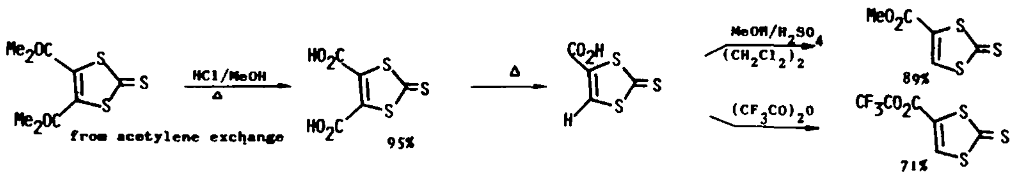
(1) The thiapentadione[23] (Scheme 105) has proven to be a versatile intermediate for the elaboration of a wide variety of tetrathiafulvalenes. The key step of these syntheses is without doubt the selective hydrolysis of one of the carbonyls of the dione **1** to give the dithiolate **2** (Scheme 105).

(2) Monodecarboxylation of 4,5-dicarbomethoxy-2-thioxo-1,3-dithiol leads[26] to 4-carboxy-2-thioxo-1,3-dithiol. The latter has been involved in the preparation of several derivatives (Scheme 106).

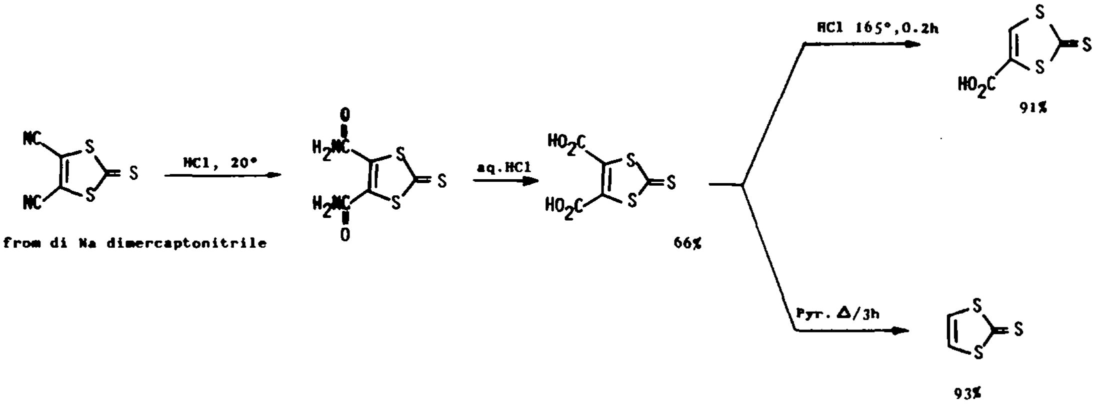
(3) Didecarboxylation of the same compound[11] allows one to efficiently obtain the 2-thioxo-1,3-dithiol using potassium cyanide and carbon disulfide (Scheme 107).



Scheme 105.[23]



Scheme 106.[26]



Scheme 107.[11]

3. CONCLUSION

In conclusion, there exists a panopoly of methods affording the 2-oxo-, 2-thioxo- or 2-selenoxo-1,3-dithiols or their 1,3-diselenol analogues. The ditellurols remain for the most part largely unexamined. The following are among the most efficient methods:

(1) The acid catalyzed cyclization of β-oxo-dialkylaminodithiocarbamates and their selenated analogues. This method has been used for the synthesis of derivatives bearing alkyl, cycloalkyl, or aryl groups and a modification of this allows access to derivatives carrying hydrogens in positions 4 and 5. The exchange reaction between an acetylene and the ethylene trithiocarbonate complements the preceding example since it affords derivatives bearing electron-withdrawing groups in the 4- and 5-positions but not those possessing alkyl groups or hydrogens in the same positions.

(2) The reaction of thiophosgene with α,β-ethylenic dithiolates is particularly efficient for the synthesis of heterocycles fused to an aromatic ring, as well as of heterocycles bearing cyano or thioalkyl groups in positions 4 or 5.

(3) Finally, the thermal decomposition of thiadiazoles and selenodiazoles affords the dithiols and diselenols fused to a 5- or 6-membered ring (including aromatic ones).

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