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Synthesis and reactions of benzo-1,3-dichalcogenoles and their derivatives

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SYNTHESIS AND REACTIONS OF BENZO-1,3-DICHALCOGENOLES AND THEIR DERIVATIVES

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A comprehensive up-to-date review of the synthesis and reactions of benzo-1,3-dithioles, benzo-1,3-diselenoles and benzo-1,3-ditelluroles is presented. An appreciable synthetic potential of these chalcogen-containing heterocycles for the preparation of dibenzotetrachalcogenafulvalenes, particularly carbonyl compounds and hydrocarbons, is displayed.

Key words: Benzo-1,3-dithioles, benzo-1,3-diselenoles, benzo-1,3-ditelluroles, dibenzotetrachalcogenafulvalenes.

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1. INTRODUCTION

Special attention has been paid in the last 15–20 years to tetrachalcogenafulvalenes (TCF) and their radical ion salts and charge-transfer complexes with various electron-acceptor compounds, in particular those with tetracyanoquinodimethane which possess high electric conductivity and even superconductivity at low temperature. Methods of preparation and reactions of TCF and their dibenzo derivatives (DBTCF) have been amply surveyed in numerous review papers.[1–7] Amongst benzoannelated TCF the most thoroughly studied are the dibenzotetrathiafulvalenes (DBTTF) whose first representative was prepared some 70 years ago.[8] In contrast, syntheses of dibenzotetraselenafulvalene (DBTSF)[9] and dibenzotetratellurafulvalene (DBTTeF)[10] were reported fairly recently. The main precursors of DBTCF are, in the case of DBTTF, benzo-1,3-dithiolylium salts (see reviews[11–14]) and benzo-1,3-dichalcogenoles (BDC). With the exception of benzo-1,3-dithioles (BDT) to which a brief section has been devoted in a review[14] of syntheses and reactions of 1,3-dithioles, no reviews are concerned with the methods of preparation and the chemical behavior of benzo-1,3-dichalcogenoles. Apart from their role as starting materials for the preparation of DBTCF, these compounds have been found to be useful synthons in various procedures leading to carbaldehydes and ketones,[15–25] tertiary alcohols,[26,27] alkanes,[28,29] and cycloalkanes.[24,25]

The purpose of the present review is to systematize the abundant and rapidly accumulating information about syntheses and reactions of BDC. The bulk of this review is concerned with methods of preparation and chemical transformations of benzo-1,3-dithioles (BDT). At the present time rather scarce data are available with regard to other BDC and corresponding benzo-1,3-dichalcogenolylium salts. Suffice it to mention that benzo-1,3-ditellurole (BDTe) was prepared in 1988[30] whereas of the simple derivatives of benzo-1,3-diselenole the only known compounds are benzo-1,3-diselenole-2-thione[9] and benzo-1,3-diselenole-2-selone.[9,31] A special section of this review is devoted to reactions of BDC leading to DBTCF. Significant success has been achieved in this area during the last years, particularly in the synthesis of the compounds with nonidentical arene rings.

LIST OF ABBREVIATIONS

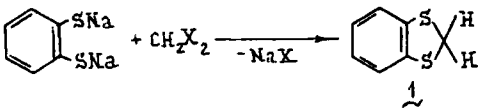
BDC benzo-1,3-dichalcogenoles
BDSe benzo-1,3-diselenoles
BDT benzo-1,3-dithioles
BDTe benzo-1,3-ditelluroles
DBTCF dibenzotetrachalcogenafulvalenes
DBTSF dibenzotetraselenafulvalenes
DBTTF dibenzotetrathiafulvalenes
DBTTeF dibenzotetratellurafulvalenes
TCF tetrachalcogenafulvalenes
TCE tetrachloroethylene

2. SYNTHESIS OF BENZO-1,3-DICHALCOGENOLES AND THEIR DERIVATIVES

The methods of preparation of BDC are classified according to: 1) the substitution in the 2-position of the heterocycle and 2) the choice of precursor for the targeted heterocycle. The basic chalcogen-containing precursors of BDC are known to be benzene-1,2-dithiols (-diselenols, -ditellurols) or their lithium and sodium salts, dithiocarbonic acids, and dithiocarbamates as well as heterocyclic compounds with built in 1,3-dichalcogenole moieties: benzo-1,3-dithiolylium salts, 2-alkoxybenzo-1,3-dithioles, and benzo-1,3-dithiole-2-ylidenes (heterocyclic carbenes).

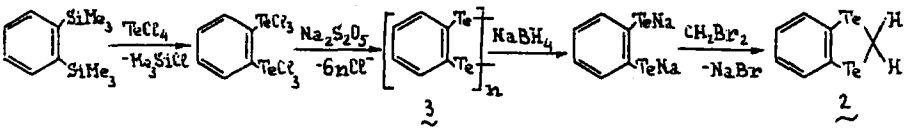
2.1. *Benzo-1,3-dichalcogenoles and Their 2-R and 2,2-R^1, R^2 Derivatives*

2.1.1. *2H-Benzo-1,3-dichalcogenoles.* The parent benzo-1,3-dithiole **1** may be prepared by either of four different methods. One of them involves coupling disodium benzene-1,2-dithiolate with diodomethane and leads to **1** in 67% yield.[32] When CD_2Cl_2 was used instead of diodomethane, the yield of 2,2-bis-(deutero)benzo-1,3-dithiole rose to 86%.[21]



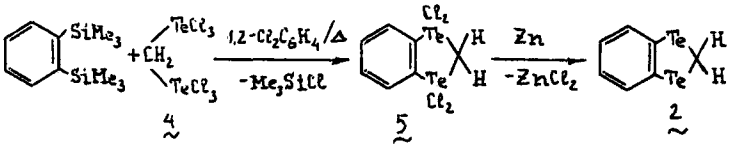
1

A similar approach was employed for the preparation of benzo-1,3-ditellurole **2**.[30,33] However, in contrast to the easily accessible benzene-1,2-dithiol, the sodium salt of its tellurium analog used as a starting material for the synthesis of **2** must be prepared according to a three-step reaction scheme based upon bis(1,2-trimethylsilyl)benzene. Disodium benzene-1,2-tellurolate is generated *in situ* by reduction of poly[(*o*-phenylene) ditelluride] **3** and affords **2** in 40–47% yield after treatment with excess dibromomethane at low temperature.



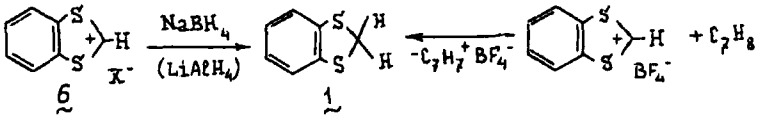
It is noteworthy that attempts to synthesize polymer **3** by reaction of *o*-diiodobenzene with Na_2Te_2 led unexpectedly to telluranthrene,[34] whereas the reaction of *o*-dibromobenzene with Na_2Se_2 afforded the selenium analog of **3**.[35]

Another route to BDTe **2** is associated with the reaction of the readily accessible bis(trichlorotelluro)methane **4**[36] with 1,2-bis(trimethylsilyl)benzene which results in the formation of 1,1,3,3-tetrachloro-BDTe **5**.[33] Reduction of **5** affords **2** in 18% yield [with respect to the starting 1,2-bis(trimethylsilyl)benzene]. Such an approach is hardly extendable to the preparation of other BDC due to the very low stability of the σ-sulfuranes and σ-selenuranes corresponding to **4**.[33]



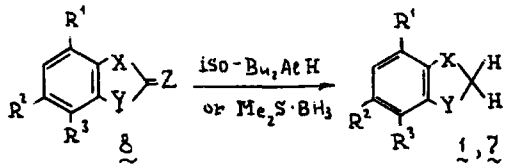
Surprisingly, no reports have yet appeared of the preparation of benzo-1,3-diselenole in spite of the fact that the synthesis of its likely precursors, dilithium benzene-1,2-diselenolate[9] and poly[(*o*-phenylene) diselenide][35] has been described.

Reduction of the benzo-1,3-dithiolylium salts **6** with $NaBH_4$[37] or $LiAlH_4$[16,17] provides a convenient method for the preparation of BDT **1** and its 2-substituted derivatives. Even cycloheptatriene can serve as the source of hydride ions in the reaction with **6**. It smoothly occurs in acetonitrile solution at 0 °C, BDT **1** being formed in 65% yield.[37,38] The salts **6** can be obtained in high yield by treatment of the readily accessible 2-alkoxybenzo-1,3-dithioles with mineral acids (see Section 3.2.).



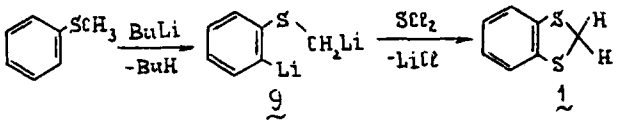
X = BF_4^-, ClO_4^-

By reduction of the thiones **8** with di(*i*-butyl)aluminum hydride or with the $BH_3 \cdot Me_2S$ complex a series of derivatives of BDT **1** containing various substituents in the arene rings have been obtained in 65–96% yield.[39] The same method proved also efficient in the synthesis of 2*H*-benzo-1,3-thiaselenole **7** (X = S, Y = Se).



X = Z = S, Y = Se, $R^1 = R^2 = R^3 = H$; X = Y = Z = S:
$R^1 = R^2 = R^3 = H$; $R^1 = R^3 = H$: R^2 = Me, NO_2, NH_2;
$R^2 = R^3 = H$, R^1 = OH; $R^2 = H$: $R^1 = R^3$ = OMe, OAc, OTs

Recently a new approach has been suggested to the synthesis of BDT **1** and other benzoannelated five-membered heterocyclic compounds with two heteroatoms.[40] The key step in these syntheses is the treatment of the organolithium compound **9**, obtained by reaction of thioanisole with excess butyllithium, with sulfur dichloride.

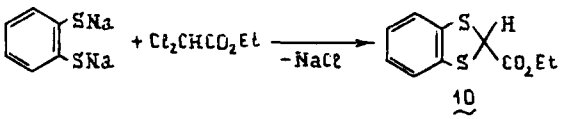


This approach is expected to be applicable to the preparation of "mixed" benzo-1,3-thiachalcogenoles: -1,3-thiaselenole (from **9** and $SeCl_2$) and -1,3-thiatellurole (from **9** and TeI_2 or elemental tellurium).

2.1.2. *2-R- and 2-R^1-2-R^2-Benzo-1,3-dichalcogenoles.* The principal synthons for the preparation of various derivatives of BDT mono- or disubstituted in the 2-position are benzene-1,2-dithiols, benzo-1,3-dithiolylium salts, and 2-alkoxybenzo-1,3-dithioles. One of the few exceptions is the untypical synthesis of perfluoro-2,2-dimethylbenzo-1,3-dithiole obtained in low yield (4%) by SbF_5 catalyzed reaction of decafluorodiphenyl sulfide with hexafluoropropylene.[41]

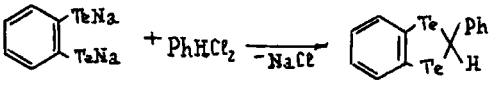
2.1.2.1. *From benzene-1,2-dichalcogenols.* There are known three main ways of preparation of BDC from benzene-1,2-dichalcogenols.

The first of these, only scarcely explored, is based on the reaction of benzene-1,2-dichalcogenols or benzene-1,2-dichalcogenolates with geminal dihalides. In the chemistry of BDT, the only reaction studied so far is that of disodium benzene-1,2-dithiolate with ethyl dichloracetate. It affords 2-carbethoxybenzene-1,3-dithiole **10** in rather low yield (23%).[42]



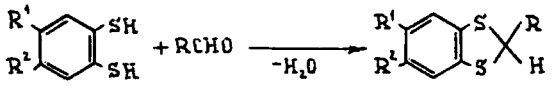
A similar reaction was utilized for the synthesis of 2-substituted derivatives of BDTe which may be exemplified by a preparation of 2-phenylbenzo-1,3-ditel-

lurole **11** in 15% yield by coupling of disodium benzene-1,2-ditellurolate with benzylidene chloride.[43]



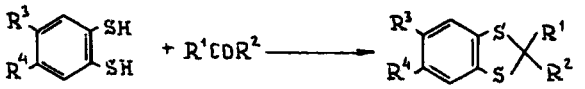
11

The most general way to derivatives of BDT is the acid-catalyzed condensation of benzene-1,2-dithiols with aldehydes and ketones giving rise to 2-R-[16,28,44-48] and 2-R^1-2-R^2 derivatives of BDT,[28,44,49] **12** and **13** in almost quantitative yields. Both protic (HCl,[44,45,48] HBF_4,[16,28,49] TsOH[28]) and Lewis ($Et_2O \cdot BF_3$[16]) acids are used to catalyze the reaction.



12

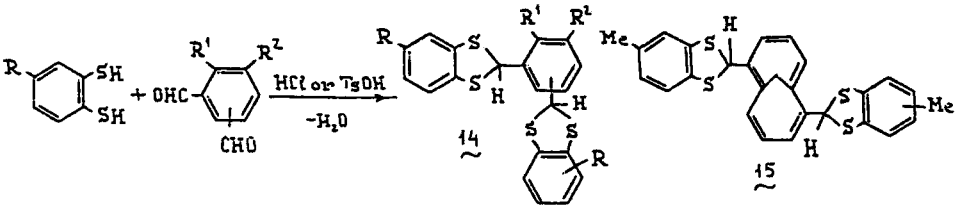
$R^1 = R^2 = H$:
R = Ph,[16,28,44] 4-$MeOC_6H_4$,[16,28,45] 4-ClC_6H_4,[16] 4-MeC_6H_4,[28] 4-HOC_6H_4,[45] 2-hydroxynaphthyl,[45] 2-$O_2NC_6H_4$,[45] 4-$Me_2NC_6H_4$,[46] PhCH=CH,[20,45] 4-$Me_2NC_6H_4CH$=CH,[46] cyclo-C_6H_{11},[16] *n*-C_9H_{19},[16,28] $C_{15}H_{31}$,[20] $PhCH_2$;[28]
$R^1 = R^2 = Me$:
R = Ph;[47]
$R^1 + R^2 = OCH_2O$:
R = 2-OCH_3, 3,4-$(OCH_2O)C_6H_2$.[48]



13

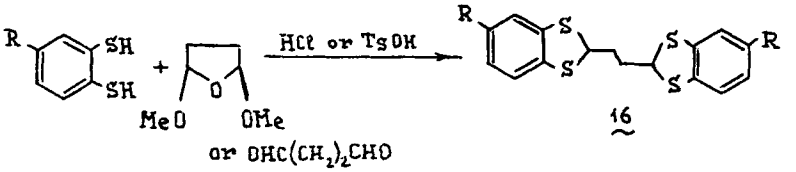
$R^3 = R^4 = H$:
$R^1 = R^2$ = Ph;[28] R^1 = Ph, R^2 = Me;[28,44]
$R^1 = C_8H_{17}$, R^2 = Me;[20,28]
R^3 = EtS, $R^4 = SC_{12}H_{25}$:
$R^1 + R^2 = (CH_2)_{11}$,[49] $(CH_2)_2CH(t\text{-}C_4H_9)CH_2$.

When bis-aldehydes are employed in this reaction, the product contains two benzo-1,3-dithiolyl moieties. From phthalic aldehydes[50-52] and naphthalene-1,4-dicarbaldehyde[53] BDT **14** are obtained in 73–93% yield whereas 1,6-methano[10]annulene-2,7-dicarbaldehyde affords BDT **15** in 72% yield.[54]



14 **15**

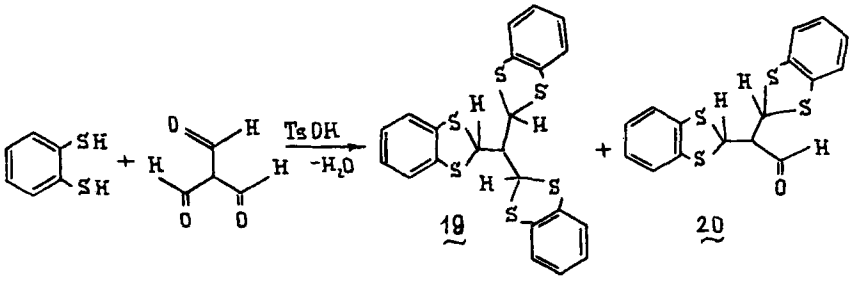
Similarly by use of succinic aldehyde[55] or 2,5-dimethoxytetrahydrofuran[55,57] the bis(1′,2′-benzo-1,3-dithiolyl-2)ethanes **16** have been prepared in high yields (70–97%).



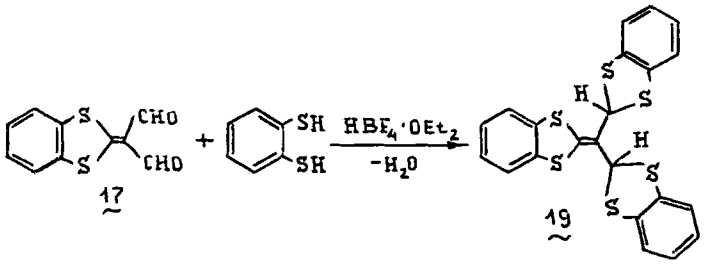
16

R = H, Me

By condensation of triformylmethane[58] or of the dialdehyde**17**[59] with benzene-1,2-dithiol tris(benzo-1,3-dithiolyl-2)methane **18** and its dehydrogenated analog **19**, respectively, have been synthesized. In the former case **19** is obtained in only 6% yield, bis(benzo-1,3-dithiolyl-2)acetaldehyde **20** being the main product (16% yield[59]).

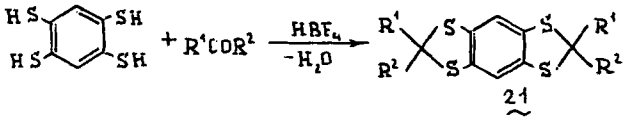


19 20



17 19

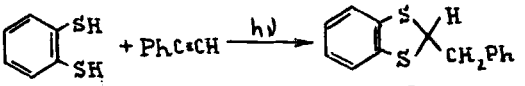
The benzo[1,2-*d*:4,5-*d*′]bis[1,3]dithioles **21** have been obtained in moderate yields by reaction of benzene-1,2,4,5-tetrathiol with carbonyl compounds in the presence of catalytic amounts of HBF_4.[49]



21

R^1 = H, R^2 = $CH_2CHMeS(CH_2)_{11}Me$;
R^1 = CH_2CHMe_2, R^2 = $CH_2CHMeCH_2CHMe_2$

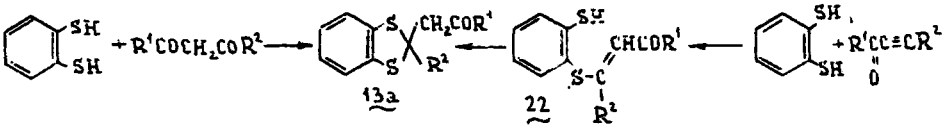
The synthesis of 2-substituted BDT is also possible via coupling of benzene-1,2-dithiols with acetylenes[60–62] or 1,3-diketones.[8] Under UV irradiation benzene-1,2-dithiol reacting with phenylacetylene affords 2-benzylbenzo-1,3-dithiole **12** in 43% yield.[60]



12

Similarly nucleophilic addition of benzene-1,2-dithiol to the triple bond of acylacetylenes[61,62] or of esters of α-acetylenic acids[61] leads to BDTs **13a**, another route to these compounds being the Brønsted acid-catalyzed reaction with 1,3-dicarbonyl compounds.[8] The intermediates of the former reaction are the β-ketovinyl sulfides **22**.[62]

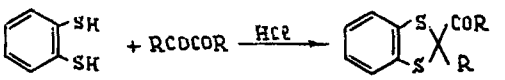
The reaction of benzene-1,2-dithiol with 1,2-diketones stops at the stage the 2-acyl-BDT **23**, whereas the second carbonyl group in **23** becomes inert to further reaction.[8]



13a **22**

$R^1 = R^2 = Me$

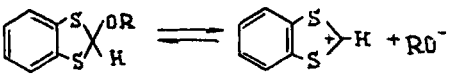
R^1 = Ph: R^2 = H,[62] Ph;[61,62] R^1 = 4-ClC_6H_4: R^2 = Ph;[61] R^1 = 2-C_4H_3S: R^2 = H, Bu, Ph;[62] R^1 = Me: R^2 = Ph, 2-C_4H_3S;[62] R^1 = OMe: R^2 = Ph, 4-ClC_6H_4[61]



23

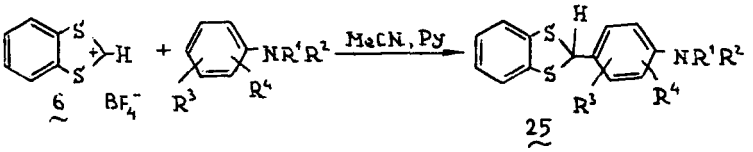
R = Me, Ph

2.1.2.2. *From benzo-1,3-dithiolylium salts and 2-alkoxybenzo-1,3-dithioles.* The high electrophilicity of the benzo-1,3-dithiolylium cation **6** as well as that (of 2-alkoxy-BDT **24**), the latter being caused by ionization in solution with formation of the dithiolylium cation,[15] provides for their smooth reactions with aromatic and heterocyclic C-nucleophiles leading to diverse 2-substituted benzo-1,3-dithioles.

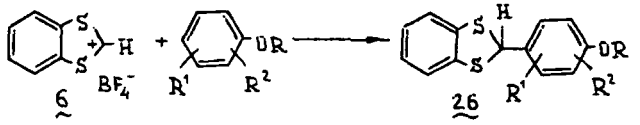


24 **6**

Thus, *N,N*-dialkylanilines,[37,50,63] naphthylamines,[37] phenols,[37,64] and naphthols[37] as well as polymethoxybenzenes[37] readily react with benzo-1,3-dithiolylium tetrafluoroborate in acetonitrile in the presence of pyridine.

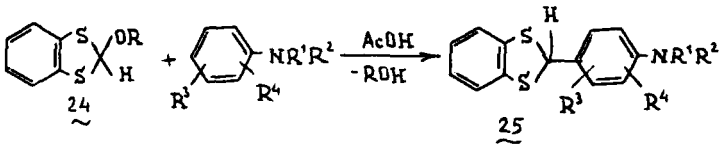


$R^1 = R^2 = Me$, $R^3 = R^4 = H$;[37]
$R^1 = H$, $R^2 = Et$, $R^3 + R^4 = 2,3\text{-}(CH{=}CH)_2$[37]

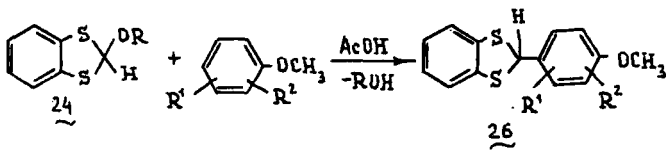


$R = Me$, $R^1 = 3\text{-}MeO$, $R^2 = 5\text{-}MeO$;[37]
$R = Ac$, $R^1 = 2\text{-}Me$, $R^2 = 6\text{-}Me$;[37]
$R = Ac$, $R^1 + R^2 = 3,4\text{-}(CH{=}CH)_2$;[37]
$R = H$: $R^1 = 2\text{-}Cl$, $R^2 = 6\text{-}Cl$.[64]

When 2-alkoxybenzo-1,3-dithioles are used, the reaction proceeds best in acetic acid solution, the yields of compounds **25** and **26** can reach 98%.[15]



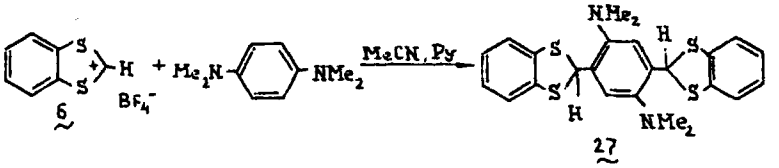
$R = n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_5H_{11}$, $n\text{-}C_6H_{11}$; $R^3 = R^4 = H$:
$R^1 = R^2 = Me$, Et, CH_2Ph; $R^1 + R^2 = (CH_2)_2O(CH_2)_2$;
$R^1 = Et$, $R^2 = C_2H_4OAc$; $R^1 = R^2 = Me$: $R^3 = H$:
$R^4 = 3\text{-}Me$, $3\text{-}MeO$, $3\text{-}OAc$; $R^3 + R^4 = 2,3\text{-}(CH{=}CH)_2$



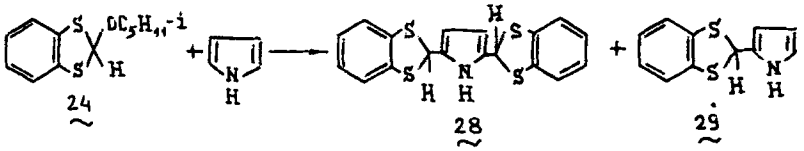
$R^1 = H$, $R^2 = 3\text{-}MeO$; $R^1 = 3\text{-}MeO$, $R^2 = 5\text{-}MeO$

At the same time *o*- and *p*-methyl-, *p*-nitro- and *p*-phenylazo-*N,N*-dimethylaniline as well as *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, *p*-dimethoxybenzene, 1-methoxynaphthalene and 1,3,5-trimethylbenzene do not react with 2-alkoxy-BDT.[15] However, by use of benzo-1,3-dithiolylium tetrafluoroborate **6**

instead of 2-alkoxy-BDT, in the reaction with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine bis(benzo-1,3-dithiole) **27** is obtained in 51% yield.[50]

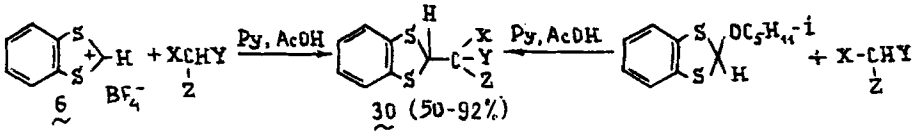


The 2- or 3-hetaryl substituted BDT have been obtained in high yields by coupling of 2-alkoxy-BDT with pyrrole and indole as well as with 1-, 2-, and 3-methylindole[65,66] and -pyrrole.[65,67] The reaction with pyrrole is peculiar.[65] When excess 2-isopentoxy-BDT **24** is allowed to react with pyrrole, almost exclusive formation of the bis-derivative **28** takes place.[65] In the case of excess pyrrole, only one electrophilic species enters the 2-position of pyrrole and **29** is formed, whereas with equimola concentrations of **24** and pyrrole an approximately 1:1 mixture of **28** and **29** is isolated.



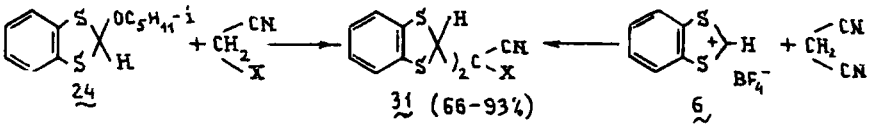
Methylene active compounds also react with benzo-1,3-dithiolylium salts **6**[37] or 2-alkoxy-BDT **24**[68] to form the 2-substituted BDT **30** and **31**. The reaction proceeds smoothly in acetic acid solution at room temperature in the presence of pyridine[37,68] or even without it.[68] In the case of 1,3-diketones and acetoacetic ester only one of the methylene group hydrogens undergoes substitution by the BDT moiety.[37,68]

By contrast, reaction of **6** and **24** with cyanoacetic esters, malononitrile, cyanoacetamide results in the substitution of both methylene protons.[37,68]



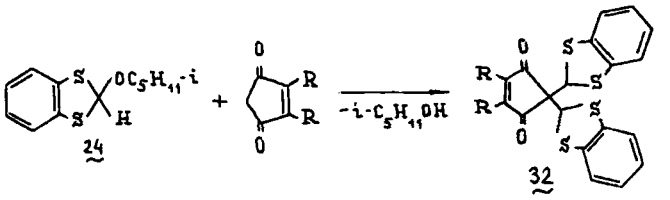
Z = H: X = Y = COMe;
X = COMe, Y = CO_2Et;
X + Y = $COCH_2CMe_2CH_2CO$

Z = H:
X = Y = COMe,
X + Y = $CO(CH_2)_3CO$,
$COCH_2CMe_2CH_2CO$;
X = COMe, Y = CO_2Et;
X = COPh, Y = CN;
X = COMe, Y = SPh;
Z = Me: X = Y = COMe;
Z = CHO:
X + Y = $CO(CH_2)_3$, $CO(CH_2)_4$



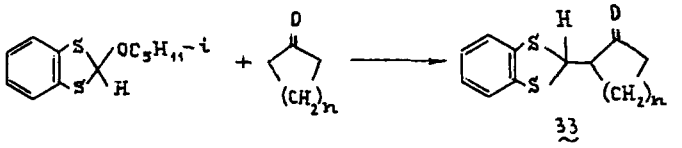
X = CN, $CONH_2$, CO_2Me

4-Cyclopentene-1,3-dione and indan-1,3-dione react with **24** in a similar manner.[69]



R = H; R + R = $(CH{=}CH)_2$

Reactions of **24** with compounds containing less acidic methylene groups, e.g. activated by only one vicinal carbonyl function, require more stringent conditions. Thus, only moderate yields of **33** have been achieved by prolonged refluxing of acetic acid solutions of **24** and cycloalkanones.[68]



n = 3 (33%), 2 (29%)

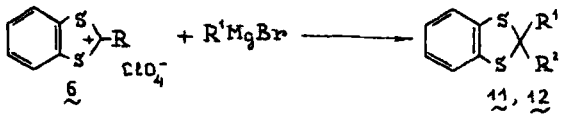
The reduction of benzo-1,3-dithiolylium salts **6** with aluminum or boron hydrides is the most common method of preparation of BDT **12**. The following hydrides have been used: $NaBH_4$,[23,28,54] $NaBD_4$,[16] $LiAlD_4$,[16] and $NaBH_3CN$,[51] the yields of **6** falling into the range 70–100%. In some cases the starting salts **6** were not isolated before their reaction with the reducing agent.

R = Ph,[16,28] 4-$MeOC_6H_4$,[16,28] 4-MeC_6H_4,[28] 4-ClC_6H_4,[16] *n*-C_9H_{19},[16,23,28] $PhCH_2$,[23,28] CH_2CMe_3,[23] *cyclo*-C_6H_{11},[16,23] $CH(Me)C_6H_{11}$-*cyclo*,[23] $CH(Me)C_8H_{17}$-*n*[23] $CH_2(PhCH_2)_2$,[23] $CH(n\text{-}C_6H_{13})_2$,[23] *cyclo*-$C_{12}H_{25}$,[23] $(CH_2)_2CH(CMe_3)(CH_2)_2CH$[23] 1-adamantyl,[23] 1-norbornyl[23]

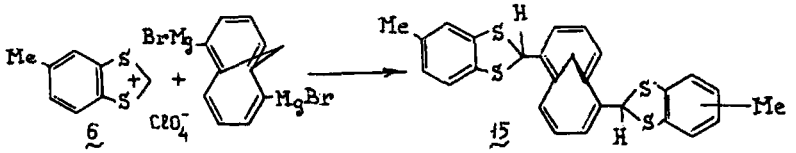
From the bis(benzo-1,3-dithiolylium) salts **35** bridged BDTs **34** have been obtained.[28,51,54]

R = $(CH_2)_{10}$,[28] *p*-C_6H_4,[51] 16-methano[10]annulene-2,7[54]

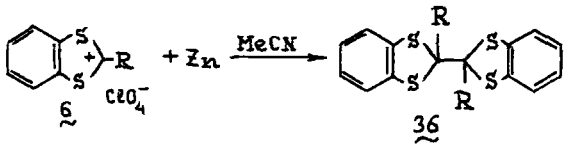
Various BDT's containing one (**12**) or two substituents (**13**) in the 2-position have been obtained in good yield by treatment of **6** with Grignard reagents.[17,21,54]



R = H: R^1 = Ph,[17] 4-$MeOC_6H_4$,[17] *iso*-C_3H_7,[17] *cyclo*-C_6H_{11};[17]
R = Ph: R^1 = Me,[17] Ph;[17] R = D: R^1 = Ph,[21] 4-$MeOC_6H_4$,[21] *n*-C_9H_{19}[21]

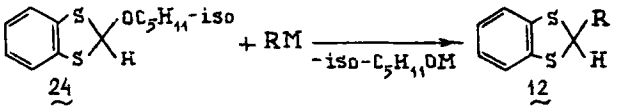


It is worth noting that in the reaction of PhMgBr with benzo-1,3-dithiolylium perchlorate the by-products isolated in small amounts are DBTTF and bis(benzo-1,3-dithiolyl-2) **36** (R = H).[17] Compound **36** (R = Ph) has been obtained in 15% and 50% yield, respectively, by treatment of 2-phenylbenzo-1,3-dithiolylium perchlorate with MeMgBr or PhMgBr.[17] The formation of **36** demonstrates the radical mechanism of the above reactions. The same mechanism obviously operates when the dimers **36** are obtained from **6** upon reduction with zinc dust in acetonitrile.[17]



R = H, Ph

Since 2-alkoxy-BDT's serve as chemical equivalents of benzo-1,3-dithiolylium in many reactions, they can also be successfully used for the preparation of 2-substituted BDT's by coupling with Grignard reagents or lithiumorganic compounds.[70] Accounting for the easy preparative access to 2-alkoxy-BDT where anthranilic acid serves as the precursor (see Section 2.2.2.), this reaction should be regarded as being of special interest for the synthesis of various 2-substituted BDT's.



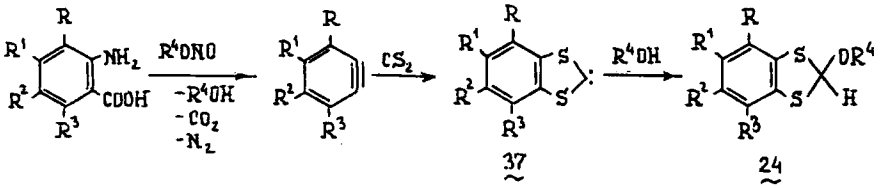
M = MgBr: R = *n*-Pr, *iso*-Pr, *cyclo*-C_6H_{11}, Ph; M = Li: R = Bu

The sulfur analogs of **24**, i.e. 2-(alkylthio)benzo-1,3-dithioles, upon treatment with butyllithium undergo deprotonation and give rise to 2-(alkylthio)-2-lithiobenzo-1,3-dithioles.[70]

2.2 *Benzo-1,3-dichalcogenoles Functionalized in the 2-Position*

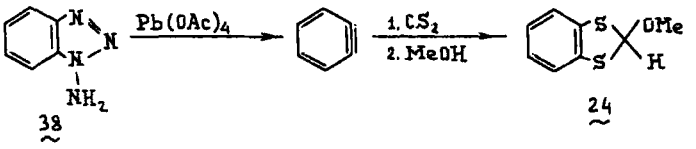
Methods of preparation of BDC's containing various functional groups in the 2-position will be considered in the following sequence: *O*- and S-derivatives, N- and P-derivatives and benzo-1,4-dithiafulvenes. No data on the synthesis of 2-halo-, -cyano-, -nitro- and otherwise substituted BDC's are yet available.

2.2.1. *O- and S-derivatives.* It has been already stressed that 2-alkoxy-BDT's **24** represent the preparatively most important group of the BDC family. The most efficient method of synthesis of **24** is addition of alcohols to benzo-1,3-dithiolecarbenes-2 **37**, obtained *in situ* by 1,3-dipolar cycloaddition of CS_2 to dehydrobenzenes.[72–76] A useful procedure has been developed for the synthesis of the latter via aprotic diazotation of anthranilic acids with alkyl nitrites and subsequent thermolysis of the arenediazonium-2-carboxylate thus formed. The reaction readily occurs with primary and secondary alkohols, the yields of **24** falling into the range 33–73%. However, attempts to utilize tertiary alcohols in this reaction were unsuccessful.[72] It is worth noting that the 2-alkoxy group of **24** can also come from the alkyl nitrite when the reaction proceeds in the absence of alcohols.



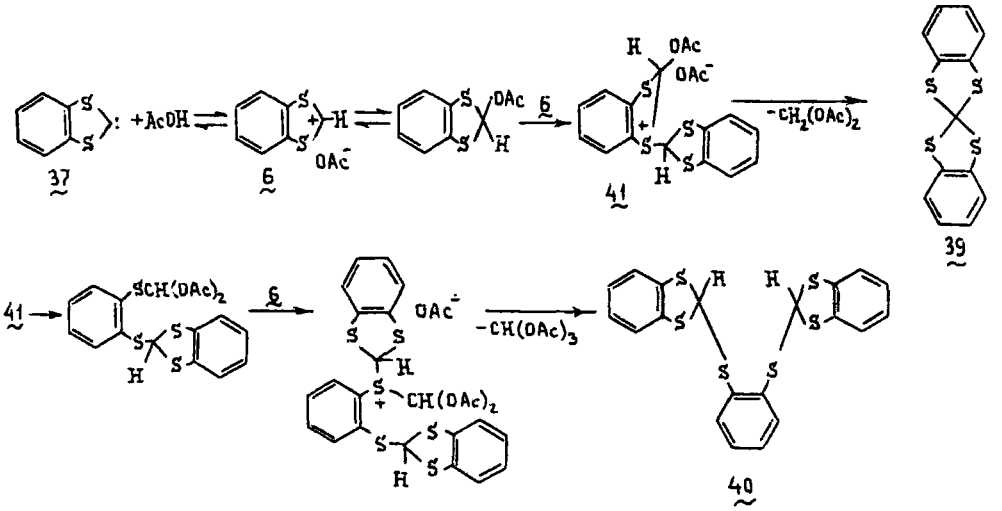
R^4 = *iso*-C_5H_{11}:
R = R^1 = R^2 = R^3 = H (below only R ≠ H shown)[72,74–76] R = Me;[75]
R^1 = Me,[75] Cl,[75] I,[75] NO_2,[75] R^1 + R^2 = $(CH{=}CH)_2$;[75]
R^1 = R^2 = R^3 = Cl,[75] Br;[75]
R = R^1 = R^2 = R^3 = H: R^4 = *n*-Pr, *n*-Bu, *n*-C_6H_{13}[72,76]

As the source of dehydrobenzene may also serve 1-aminobenzotriazole **38** upon oxidation with lead tetraacetate in 1:1 CS_2-methanol solution. 2-Methoxy-BDT has been prepared in 78% yield by this reaction.[77]

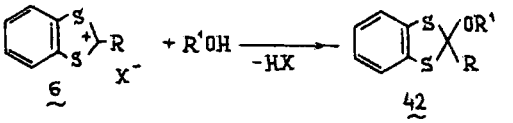


When the aprotic solvent dichloromethane is used instead of methanol the reaction proceeds in a quite different direction and results in the formation of 2,2'-spiro-bis(benzo-1,3-dithiole) **39** and 2,2'-(*o*-phenylenedithio)-bis(benzo-1,3-dithiole) **40**.[73,77] The following reaction scheme[77] has been suggested to account for the course of the reaction (acetic acid reacting with carbene **37**, the product of oxidation of **39** by lead tetraacetate).

Synthesis of BDT **24** by reactions of benzo-1,3-dithiolylium salts with alcohols,



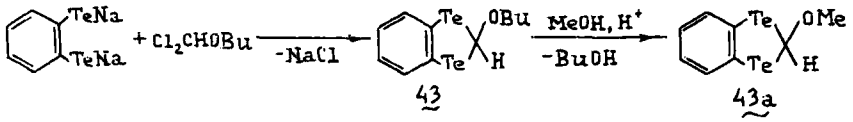
even though these occur with high yields, is of little preparative importance.[37,78,79] However, these reactions[79] may be successfully applied for the preparation of 2-alkoxy-BDT's **24** containing tertiary alkyl groups[79] and 2-R-2-(alkoxy)benzo-1,3-dithioles **42**.[78]



X = BF_4^-: R = H: R^1 = Me,[37] Et,[37] *n*-Pr;[37]
iso-Pr,[79] *t*-Bu;[79] X = ClO_4^-: R = Ph: R^1 = Et[78]

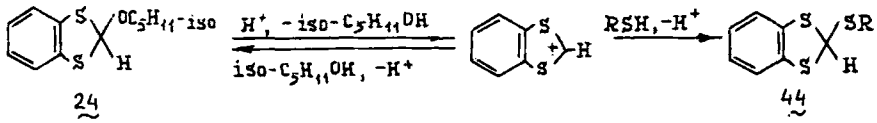
No attempts to prepare 2-alkoxy-BDT's **24** by reaction of benzene-1,2-dithiols with the readily accessible dichloromethyl alkyl ethers Cl_2CHOR have yet been undertaken. However, recently a similar approach has been employed for the

synthesis of the first representative of the 2-alkoxy-benzo-1,3-ditelluroles, 2-butoxy-BDTe **43**.[80] Compound **43** was obtained in 24% yield.



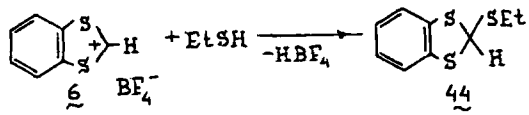
Since the tellurium analog of carbon disulfide, carbon ditelluride CTe_2, is unknown, the reaction of benzene-1,2-ditellurolates with the readily accessible dichloromethyl butyl ether acquires preparative significance considering in particular that the 2-butoxy substituent in **43** may be readily replaced by other alkoxy groups. Thus, when **43** was allowed to stand in methanol solution containing trace amounts of HBF_4 for half an hour, **43a** was obtained in more than 90% yield.[80] A similar approach seems to allow the synthesis of 2-alkoxy-benzo-1,3-diselenoles, whose preparation by use of the highly toxic carbon diselenide CSe_2 would lead to considerable difficulties.

2-Alkoxy-BDT's **24** readily exchange their 2-alkoxy group for an alkylthio group when treated with thiols in acetic acid solution.[81] 2-Alkylthio-BDT's and -arylthio-BDT's **44** have been obtained by this reaction in 70–90% yield. The reaction most probably follows a dissociative mechanism with intermediate formation of the cation **6**.

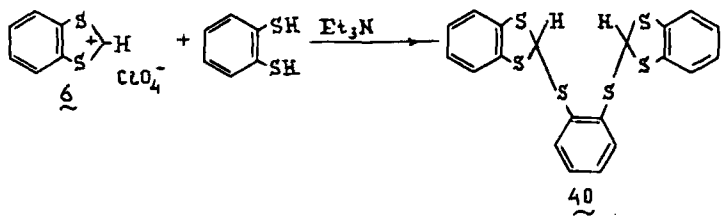


R = Et, *n*-Pr, $PhCH_2$, *cyclo*-C_6H_{11}, Me(Et)CH, *t*-Bu, Ph, 4-MeC_6H_4, 4-ClC_6H_4

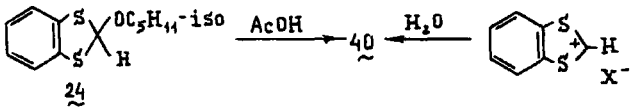
Such a mechanism is corroborated by the proneness of benzo-1,3-dithiolylium salts such as **6** to react with thiols to form **44** in high yields.[37]



With benzene-1,2-dithiol, 2,2'-(*o*-phenylenedithio)-bis(benzo-1,3-dithiole) **40** is obtained.[82]

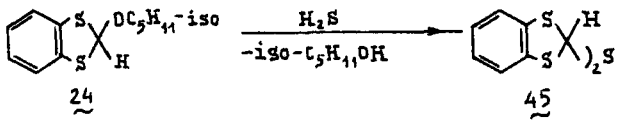


Compound **40** can also be prepared in high yield by treatment of 2-alkoxy-BDT's with acetic acid[15] or via hydrolysis of benzo-1,3-dithiolylium salts.[37,82–84]



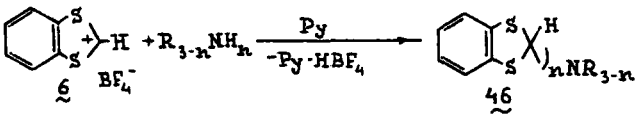
X = BF_4^-, ClO_4^-

When hydrogen sulfide is used instead of alkanethiols in the reaction with **24** the sulfide **45** is formed in high yield.[81] It is also formed as a minor product in admixture with 2-methoxy-BDT in the reaction of benzo-1,3-dithiolylium tetrafluoroborate **6** with sodium sulfide or hydrosulfide in methanol.[37]



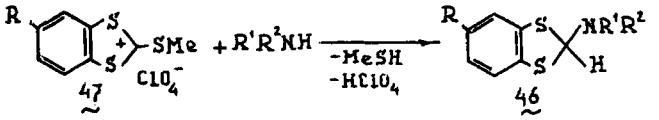
2.2.2. *N- and P-derivatives.* Benzo-1,3-dithiolylium salts serve also as the main precursors of nitrogen-centered 2-substituted BDT's. By coupling of benzo-1,3-dithiolylium tetrafluoroborate with ammonium acetate or primary and secondary amines in the presence of pyridine the compounds **46** are obtained in high yields.[37,85]

If, however, the attack of **6** at the amino nitrogen is subject to steric hindrance as is the case of *N*-ethyl-1-naphthylamine,[37] the electrophilic species **6** attacks the *p*-position with respect to the amino group (see Section 2.1.2.). It has been reported[85] that in the reaction of benzo-1,3-dithiolylium perchlorate with secondary amines 2,2'-(*o*-phenylenedithio)-bis(benzo-1,3-dithiole-2) **40** is formed along with the expected N-derivatives, their ratio depending on the structure of the secondary amine.



n = 3, n = 2: R = Ph, $PhCH_2$; n = 1: R = $PhCh_2$, *iso*-Pr, $(CH_2)_5$; R = Ph, Me

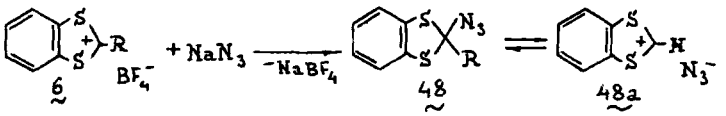
The N-derivatives **46** (n = 2) have also been prepared by coupling of various secondary amines with 2-(alkylthio)benzo-1,3-dithiolylium perchlorate **47** in THF.[86] The greater the basicity of the amine, the higher yields were achieved of **46**.



R = H, Me: $R^1 = R^2$ = Me, Et, *n*-Pr, Ph;
$R^1 + R^2 = (CH_2)_5$, $O(CH_2)_4$, R^1 = Ph, R^2 = Me; R = H: R^1 = Et, R^2 = Ph;
$R^1 + R^2$ = CHMeCH$_2$CH$_2$CHMe; R = Me: $R^1 = R^2$ = *n*-Bu

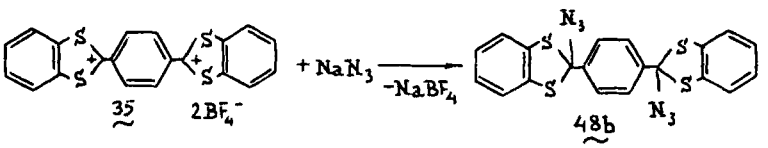
The reaction of tertiary amines with **6** leading to DBTTF will be considered in Section 4.

Of particular interest is the reaction of **6** with sodium azide in boiling toluene, resulting in the formation of 2-azido-BDT **48** in almost quantitative yield.[87,88] The covalent structure **48** has been suggested for these compounds by consideration of their ^{13}C NMR spectra. However, the broadening of the 2-C signal with rising temperature may indicate the existence of an ionization equilibrium **48** ⇌ **48a**.[87]

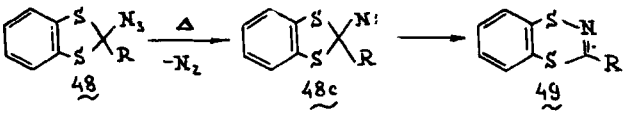


R = H, Ph, 4-MeOC$_6$H$_4$

With the bis(benzo-1,3-dithiolylium) salt **35** the reaction with sodium azide results in the *p*-phenylene bridged bis-azide **48b**.[88]

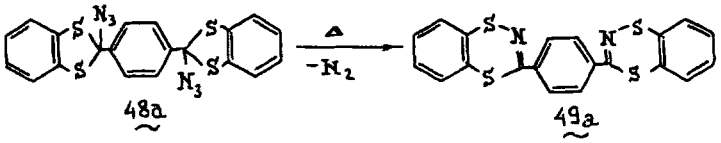


2-Azido-BDT's **48** serve as useful synthons for the preparation of 1,4,2-benzodithiazines **49**. The thermolysis of **48** is smooth and leads to **49** in high yields.[88] The reaction mechanism is most probably intermediate formation of the nitrene **48c** and subsequent intramolecular insertion into the C-S bond.



R = H, Ph, 4-MeOC$_6$H$_4$, 4-Me$_2$NC$_6$H$_4$, 3-indolyl, morpholino, MeS

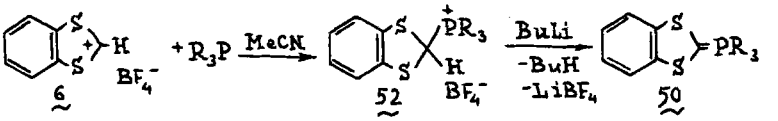
In a similar way thermolysis of **48b** gives rise to *p*-bis(benzo-1,4,2-dithiazinyl-3)benzene **49a** in 84% yield.[88]



48a 49a

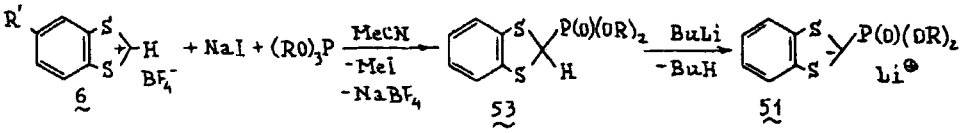
When the benzo-1,3-dithiolylium salts used for the preparation of **48** possess an electron-releasing substituent in the 2-position, the entire **6** → **48** → **49** process can be carried out as a one-pot reaction of **6** with NaN_3 in boiling toluene.[88]

The phosphonium salts **52** are obtained in high yield when the benzo-1,3-dithiolylium salts **6** are treated with phosphines in acetonitrile. Compounds **52** can be transformed to the phosphonium ylides **50**[89–95] which serve as precursors of benzo-1,4-dithiafulvenes, DBTTF, and their vinylogs. Instead of **50** the stabilized carbanions **51**,[23–25,89–91,93,96–98] obtaining by deprotonation of 2-(dialkoxyphosphinyl)benzo-1,3-dithioles **53**, can be used for the preparation of the above-mentioned species.



6 52 50

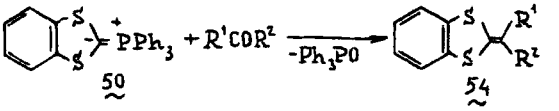
R = *n*-Bu, Ph



6 53 51

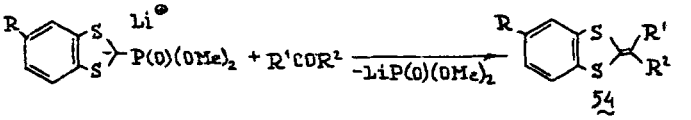
R = Me, Et; R¹ = H, Me

2.2.3. *Benzo-1,4-dithiafulvenes.* A broad variety of benzo-1,4-dithiafulvenes **54** has been obtained by treatment of aldehydes and ketones with either the phosphonium ylides **50**[89–91] or the carbanion **51**[23–25,89–91,96–98]



50 54

R¹ = H: R² = Ph,[89,91] 4-$MeOC_6H_4$,[89,91] 4-MeC_6H_4,[89,91] PhCH=CH[89,91]

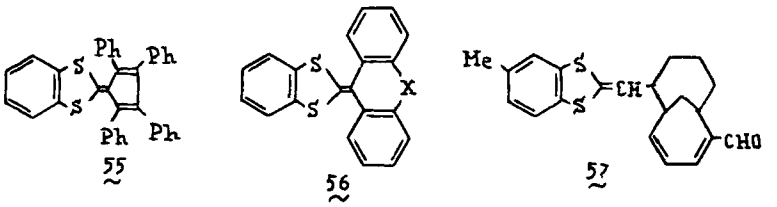


54

R = H: R^1 = H:
R^2 = 4-MeC_6H_4,[89,91] MeCH=CH,[89,91] 4-$Me_2NC_6H_4$,[91] *t*-Bu,[23] *n*-C_8H_{17},[23] Ph,[23] $PhCH_2CH_2$,[24,25] 3,4-$(MeO)_2C_6H_3CH_2CH_2$,[24,25] 2,3-$(MeO)_2C_6H_3CH_2CH_2$,[24,25] 3,4-$(OCH_2O)C_6H_3CH_2CH_2$,[24,25] 3-$MeOC_6H_4CH_2CH_2$,[24,25] 4-$MeOC_6H_3CH_2CH_2$,[24,25] 2,5-$(MeO)_2C_6H_3CH_2CH_2$,[24,25] (for additional 3-aryl-propanals, see[25]);
R^1 + R^2 = $(CH_2)_4$,[89,91] $(CH_2)_5$,[23,89,91] $(CH_2)_{11}$,[23] $(CH_2)_2CH(tBu)(CH_2)_2$,[23] CH = $CMeCH_2CMe_2CH_2$;[91]
R^1 = Me: R^2 = PhCH=CH,[91] Ph,[91] 4-MeC_6H_4,[89,91] 4-ClC_6H_4,[91] 4-$MeOC_6H_4$,[91,96] *cyclo*-C_6H_{11},[23] *n*-C_8H_{17};[23]
R^1 = R^2 = Ph,[91,96] $PhCH_2$,[23] *n*-C_6H_{13},[23] 1-adamantyl,[23] 1-norbornyl[23]

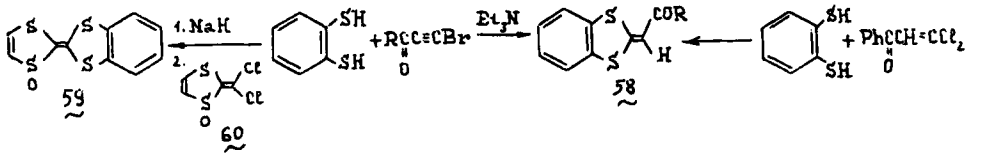
The second procedure is considered to be preferable for preparative purposes[89,91] because of the easy purification of the products and the higher thermodynamic stability of the starting **53** compared to **52**.

Among the derivatives of benzo-1,4-dithiafulvenes prepared by these reactions and potentially interesting as donor components of charge-transfer complexes with high electric conductivity are the compounds **55**,[91,96] **56** (X = bond,[91,96] CH = CH,[91,96] O,[91,96] S,[91,96] SO,[91] SO_2,[91] NMe,[91,96] NEt[91]), and **57**[97]



55 **56** **57**

Other methods for the synthesis of benzo-1,4-dithiafulvenes have of less general applications. They may be grouped into four different types. The first one involves reactions where the double bond is incorporated into a molecule simultaneously with the formation of the 1,3-dithiole moiety. In this case benzene-1,2-dithiols serve as the appropriate synthons.[62,99] Thus, the 1,4-dithiafulvenes **58** have been prepared in high yields by reaction of benzene-1,2-dithiol with either α-bromo acetylenic ketones or β,β-dichlorovinyl ketones in the presence of Et_3N.[62] The 1,4-dithiafulvene **59** is obtained from benzene-1,2-dithiol and the sulfoxide **60**[99]

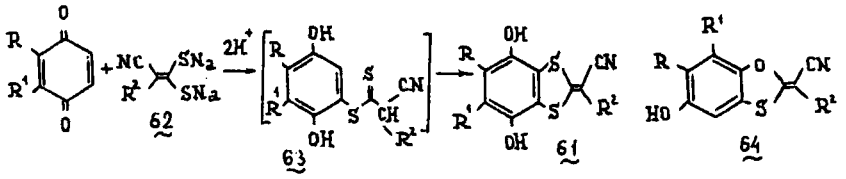


59 **60** **58**

R = Ph, α-C_4H_3S

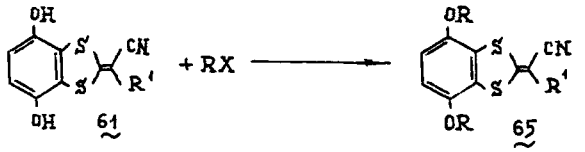
If no strong electron-withdrawing group is attached to the triple bond, the reaction proceeds less smoothly. Thus, treatment of sodium or lithium benzene-1,2-dithiolate with α-bromoacetylenes affords multicomponent mixtures from which 2-benzylidenebenzo-1,3-dithiole and 2-(α-bromobenzylidene)benzo-1,3-dithiole have been isolated in low yields.[60]

Another approach to benzo-1,4-dithiafulvenes involves the use of 1,1-ethenedithiolates as building blocks for the BDT moieties. This is accomplished either by addition of 1,1-ethenedithiolates[62] to the C=C bond of benzoquinones in acetic acid solution at 0 °C with subsequent cyclization of the primary adduct[100] or by substitution of activated halogen atoms.[100–102] The yields of **61** lie in the range 27–87%. The intermediates **63** may undergo a side reaction, elimination of H_2S, which leads to the formation of benzoxathioles **64**. Their formation is favored by a large excess of acetic acid at elevated temperatures.[100]

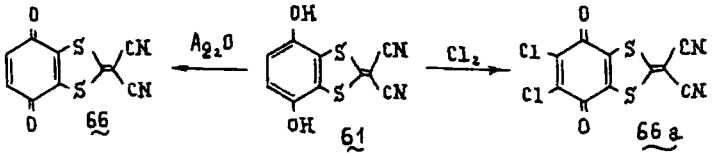


$R = R^1 = H$: $R^2 = CN, CO_2Me, CONH_2$;
$R = Me$, $R^1 = H$: $R^2 = CN$; $R + R^1 = (CH=CH)_2$, $R^2 = CN$

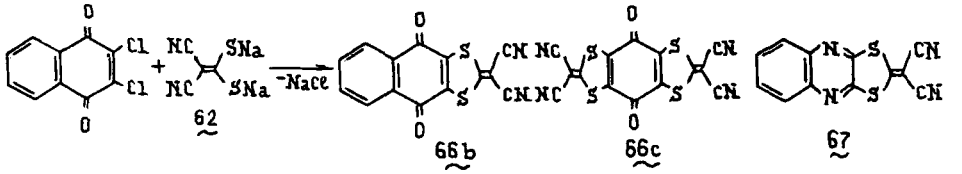
By alkylation of **61** the benzodithiafulvenes **65** have been obtained, whereas oxidation and chlorination reactions lead to the corresponding products **66** and **66a**.[100]



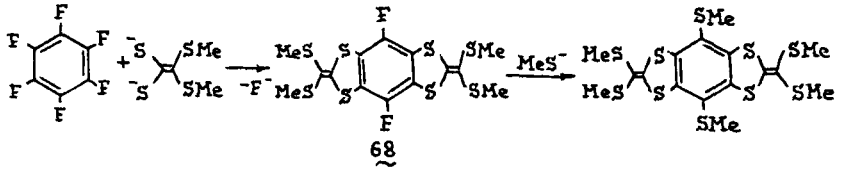
$R^1 = CN$: $R = Me, CH_2Ph$; $R^1 = CONH_2$: $R = Me$

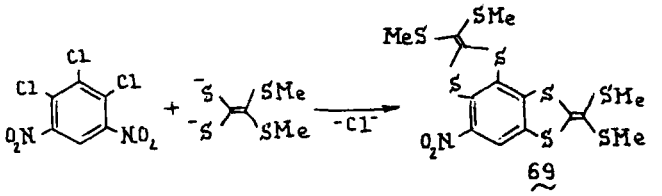


Nucleophilic substitution as access to benzo-1,4-dithiafulvenes is exemplified by the reaction of **62** ($R^2 = CN$) with 2,3-dichloro-*p*-benzoquinone.[100] Similarly, the 1,4-dithiafulvenes **66c** and **67** have been obtained from chloranil and 2,3-dichloroquinoxaline, respectively.[100]

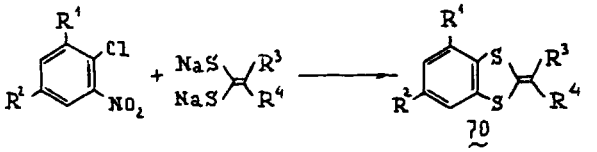


Compounds **68** and **69** are additional examples of benzo-1,4-dithiafulvenes containing two BDT moieties in a molecule. They have been obtained by coupling 2,2-bis(methylthio)ethene-1,1-dithiolate with hexafluorobenzene (41% yield) and 2,3,4-trichloro-1,5-dinitrobenzene (yield 65%), respectively.[101]



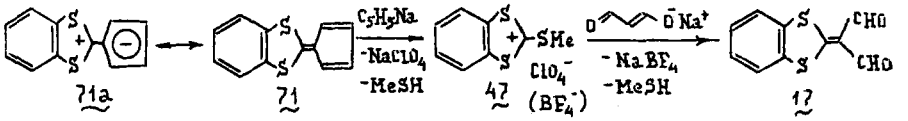


When various chloronitrobenzenes are treated with 1,1-ethenedithiolates, one of the nitro groups is lost, as was also the case in the preceding reaction, and cyclization takes place to form benzo-1,4-dithiafulvenes **70** in 11–98% yield.[101–102]



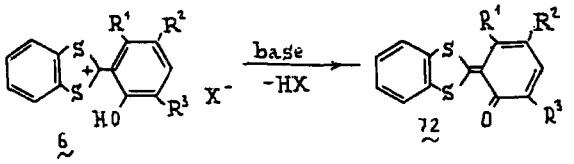
R^3 = CN: R^2 = NO_2: R^1 = H, NO_2: R^4 = CN, CO_2Me, CO_2Et;[102]
R^1 = R^2 = NO_2, R^4 = $CONH_2$[102]; R^3 = R^4 = SMe: R^2 = H, R^1 = Cl, NO_2[101]

A third approach to benzo-1,4-dithiafulvenes employs benzo-1,3-dithiolylium salts as starting materials.[58,103,104] By reaction of 2-(methylthio)benzo-1,3-dithiolylium perchlorate **47** with sodium cyclopentadienide the first known benzo-1,4-dithiafulvene **71** was obtained in 30% yield.[103] Its high stability is due to a substantial contribution of the polar resonance structure **71a**.

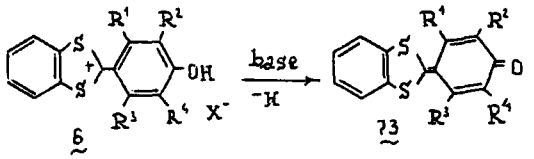


With the sodium enolate of malonic dialdehyde 6,6-diformyldithiafulvene **17** was obtained in 45% yield in the same way.[58]

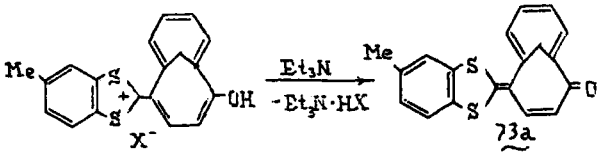
Finally, the synthesis of the *o*- and *p*-quinone methides[72,73] as well as that of their aza analogs **74** and **75** should be mentioned. It is based on the deprotonation of benzo-1,3-dithiolylium cations possessing acidic groups (OH,[45,64,105,107] NH,[66,67] or NH_2[108]) in the 2-aryl substituent by treatment of their solutions with various bases: NaOH,[45] K_2CO_3,[45] pyridine,[105] triethylamine,[64,66,106,107] and DBU.[67,108]

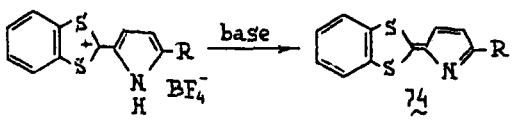


$R^1 + R^2 = (CH=CH)_2$, $R^3 = H$;[45,105] $R^1 = H$:
$R^2 = R^3 = Me$,[64] Cl[64], *t*-Bu[64,105]

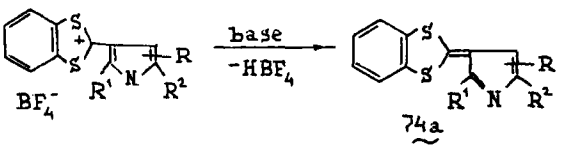


$R^1 = R^2 = R^3 = R^4 = H$;[45] $R^1 = R^3 = H$:
$R^2 = R^4 = Cl$,[64] *i*-Pr,[64] *t*-Bu,[64,105] $R^1 + R^2 = R^3 + R^4 = (CH=CH)_2$[105]

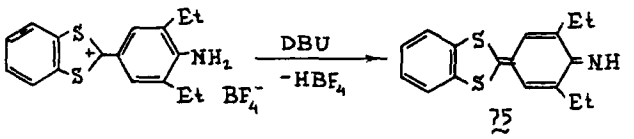




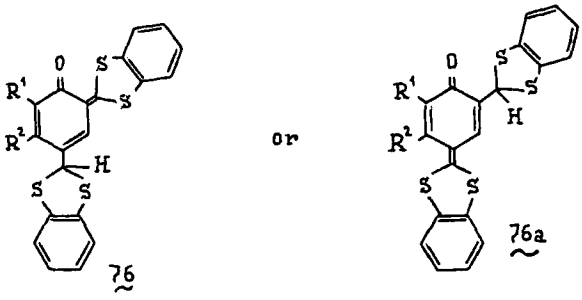
R = H, 2-(benzo-1,3-dithiolyl)



$R^1 = R^2$ = Me: R = H, 2-(benzo-1,3-dithiolyl);[67] R + R^2 = $(CH=CH)_2$: R^1 = Me,[66] R = H, 3-(benzo-1,3-dithiolyl-2)[67]

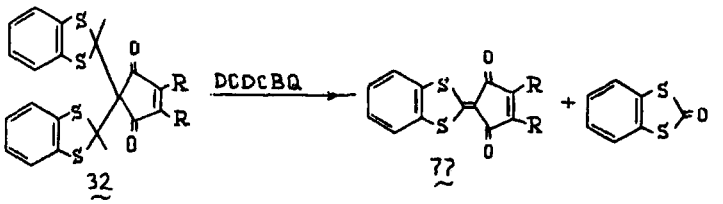


In some cases it is possible to avoid the use of preformed 2-substituted benzo-1,3-dithiolylium salts by letting them form in the preparation of the quinone methides by the coupling of two moles of a benzo-1,3-dithiolylium[64] or a 2-(methylthio)benzo-1,3-dithiolylium salt[105] with phenols and aromatic or heterocyclic amines (the second mole of the dithiolylium salt effects the dehydrogenation of the intermediate 2-substituted BDT). The reaction mixture is treated with a basic reagent to generate quinone methides. Such a procedure has been employed for the preparation of **76**[64] containing two BDT moieties in the molecule. Obviously, three moles of benzo-1,3-dithiolylium tetrafluoroborate must be employed in this reaction.

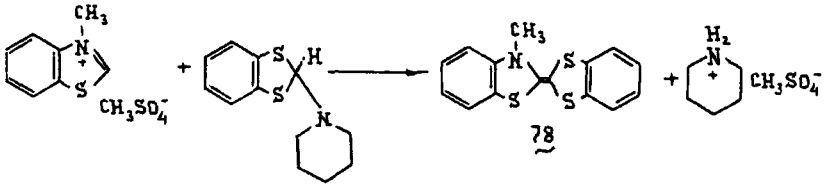


R^2 = H: R^1 = Me, Cl; $R^1 + R^2 = (CH=CH)_2$

Other methods for the synthesis of benzo-1,4-dithiafulvenes described in the literature are not generally applicable. Examples worth mentioning are the preparation of **77** by oxidation of BDT **32** with dichlorodicyanobenzoquinone[69] and of **78** from 2-piperidino-BDT by treatment with *N*-methylbenzothiazolium methyl sulfate.[109,110]

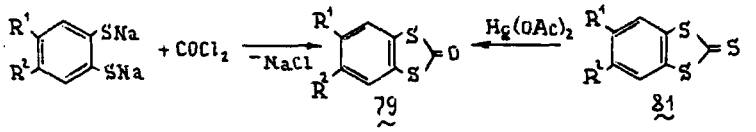


R = H, $(CH=CH)_2$



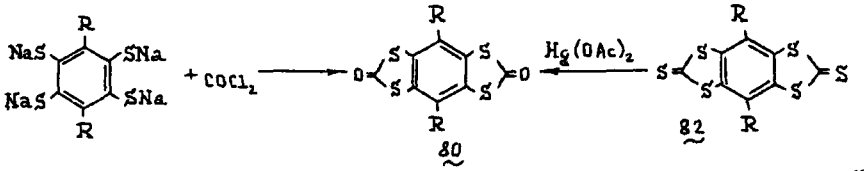
2.2.4. *Benzo-1,3-dichalcogen-2-ones (-thiones, -selones).* A variety of methods for the synthesis of these compounds have been developed, BDC-2-ones and BDC-2-thiones having been studied most thoroughly.

2.2.4.1. *Benzo-1,3-dithiol-2-ones.* Condensation of benzene-1,2-dithiolates and benzene-1,2,4,5-tetrathiolates with $COCl_2$ leads to BDT-2-ones **79**[44,47] and **80**.[111]



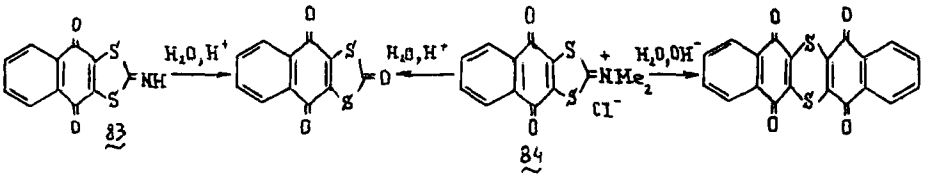
$R^1 = R^2 = H$,[41] Me[47]

Various BDT-2-ones have been prepared by transformation of BDTs functionalized in the 2-position, e.g. by oxidation of the thiones **81** and **82** with

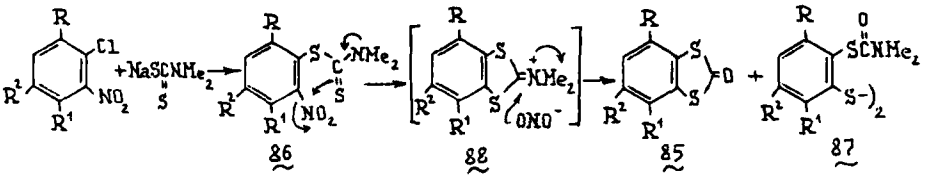


R = H[111] R = SMe, SC_5H_{11}[113]

mercury acetate[112,113] which provides **79** and **80** in 71–89% yield and by acid hydrolysis of 2-imino- (**83**) or 2-immonio-BDT **84**.[114] It is noteworthy that alkaline hydrolysis of **84** results in the formation of the corresponding thianthrene derivative.[114]



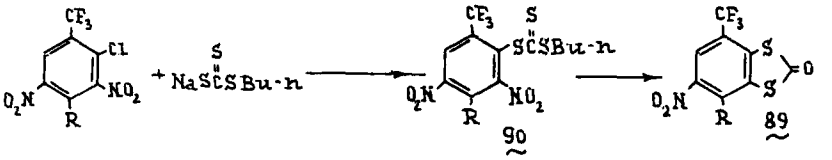
A general method for the preparation of BDT containing aromatic nitro groups is the thermal cyclization of the *N,N*-dimethyldithiocarbamates **86**.[115–117] The compounds **86** obtained by coupling 1,3-dinitrochlorobenzenes with sodium dithiocarbamate were not isolated and underwent spontaneous transformation to **85** due to a readily occurring intramolecular nucleophilic substitution, a nitro group serving as a nucleofugue. It has been found that the disulfides **87** are by-products in this reaction.[116]



R^1 = H: R = NO_2:
R^2 = CF_3 (43%), NO_2 (35%), CN (46%), F (37%), H (43%), Me (26%);
R^2 = NO_2: R^1 = H: R = CF_3 (11%), H (5%); R = CF_3:
R^1 = Me_2N (77%), Et_2N, Pr_2N, PrNH, $N(CH_2CH{=}CH_2)_2$, Bu_2N, NHBu, NHPr-*i*, NHPh, *N*-pyrrolidino, *N*-morpholino, NHMe (37–57%);
R^1 = SPr, SPr-*i* (59–61%)

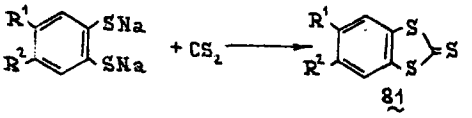
The thermal stability of the 2,4-dinitrophenyl dithiocarbamates **86** (R^2 = NO_2) is higher than that of their 2,6-dinitrophenyl isomers **86** (R = NO_2). Whereas the latter compounds are difficult to isolate because of spontaneous cyclization to benzo-1,3-dithiole-2-ones **85** at 15–20 °C, the former afford **85** in low yields under rather severe conditions. The yields, however, are increased when strongly electron-releasing substituents such as dialkylamino group (R^1 = NR_2) is present on the benzene ring. The growing interest in the synthesis of **86** is associated with the fact that some of them exhibit fungicidal activity.[117]

The benzo-1,3-dithiole-2-ones **89** have been prepared by cyclization of *n*-butyl-trithiocarbonates **90** by heating in acetic acid or DMSO.[118] It is noteworthy that cyclization of *t*-butyl trithiocarbonates leads to nitrobenzo-1,3-dithiole-2-thiones.[118]



R = H (33%), NMe_2 (31%)

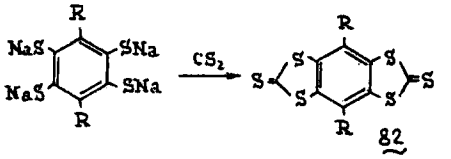
2.2.4.2. *Benzo-1,3-dichalcogenole-2-thiones.* A long known efficient method for the preparation of benzo-1,3-dithiole-2-thiones **81** is based on the reaction of disodium benzene-1,2-dithiolate with carbon disulfide.[44,47,48,112,119–121] The yields amount to 72–100%.



81

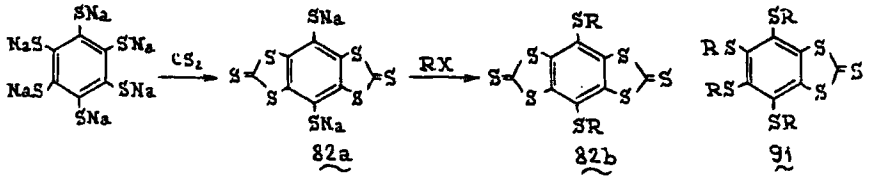
$R^1 = R^2 = H$,[44] Me;[47,112] R^1 = H: R^2 = OMe,[120] OET,[120,121] Me;[119] $R^1 + R^2 = OCH_2O$[47]

Starting with benzene-1,2,4,5-tetrathiolates the 4,8-R_2-1,3,5,7-tetrathia-*s*-indacene-2,6-dithiones **82** have been synthesized in high yields.[122–124]



82

R = H, Pr-*i*

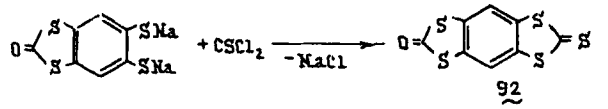


82a **82b** **91**

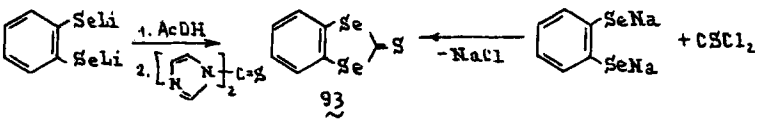
R = H, Me, *n*-C_5H_{11}, $PhCH_2$, CH_2CO_2Na, RCO (R = Me, Ph)

The compounds **82a** are obtained in quantitative yield when carbon disulfide is used in excess. With equimolar amounts of the reagents the thiones **82** and **91** are formed.[124]

The thione function may be introduced by treatment of disodium benzene-1,2-dichalcogenolates with thiophosgene (**92** and **93** have been prepared in 62% and 23% yields, respectively[111,34]). Another synthesis of **93** was carried out with 56% yield by reaction of dilithium benzene-1,2-diselenol with bis(1-imidazolyl)thione.[9]

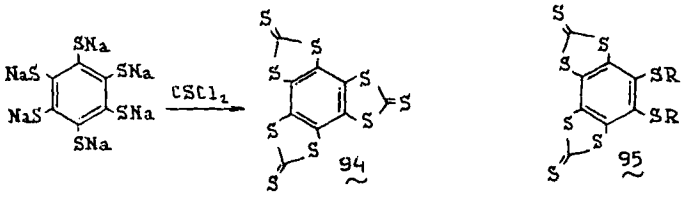


92



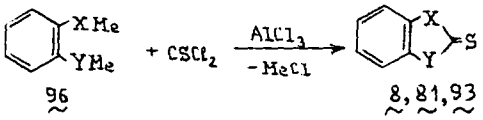
93

By reaction of thiophosgene with hexasodium benzenehexathiolate 2,5,8-trithioxobenzo[2,3]dithiole **94** was obtained in 43% yield.[125] By contrast, reaction of benzenehexathiol with carbon disulfide in pyridine solution results, after treatment with alkyl iodides, in **95** in yields in the range 54–85%.[124]



R = Me, Et, n-C_5H_{11}; R + R = CH_2

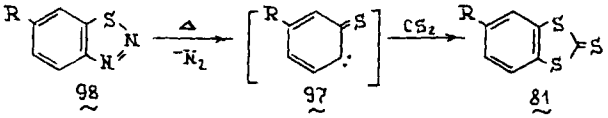
It has been shown that instead of the easily oxidized benzene-1,2-dichalcogenolates the alkyl derivatives of benzene-1,2-dichalcogenols **96** can be used to prepare the thiones **8**, **91**, and **93**.[126] This reaction occurs in 20–30% yield in the presence of $AlCl_3$.



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

When the 2-methylchalcogeno(methyltelluro)benzenes **96** (X = S, Se, Y = Te) were treated with thiophosgene[126] under similar conditions, not thiones but rather telluronium salts were obtained whose structure was not fully elucidated. Taking into account the tendency of Te(II) compounds to undergo oxidative addition reactions which convert them to stable Te(IV) derivatives, the suggestion can be made that σ-telluranes with -$TeMeCl_2$ groups are formed in this reaction.

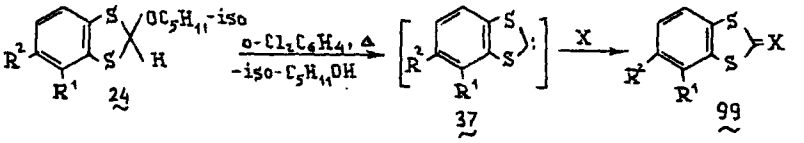
The next method of preparation of benzo-1,3-dithiole-2-thiones **81** involves 1,3-dipolar addition of a thioketocarbene **97**, generated by thermal decomposition of a 1,2,3-benzothiadiazole **98**, to the C=S bond of carbon disulfide.[127–130] The yields of **81** are reasonably high (about 80%), but the reaction requires high pressure and is therefore not useful for preparative application.



R = H,[127–130] OEt,[129] Cl,[129] NO_2[129]

Recently a useful approach to the synthesis of benzo-1,3-dithiole-2-thiones (and -2-selones) was suggested based on the reaction of benzo-1,3-dithiole-2-

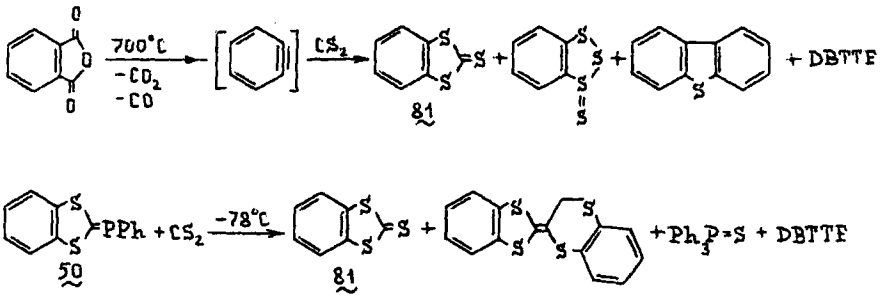
carbenes **37** with elemental sulfur and selenium.[131] Among the three methods known to generate the carbenes **37**, i.e. thermal dissociation of 2-alkoxy-BDT **24**, deprotonation of the benzo-1,3-dithiolylium cation, and cycloaddition of carbon disulfide to dehydrobenzene, the first proved to be the most efficient. Reflux of a *o*-dichlorobenzene solution of 2-isopentoxy-1,3-dithiole **24** with elemental sulfur or selenium gives the thiones **99** (X = S) in 55–95% yield or the selones **99** (X = Se) in 43–87% yields.[131] Carbenes with enhanced nucleophilicity due to the presence of electron-releasing substituents on the benzene ring react more smoothly and afford higher yields of **99**. However, in all cases a certain amount of DBTTFs due to dimerization of the carbenes **37** is formed.[131]



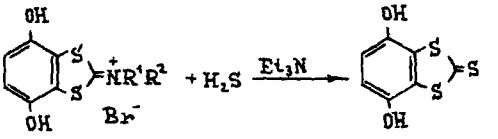
X = S: $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$;
$R^1 = H$: $R^2 = Me$, Cl, NO_2; X = Se: $R^1 = R^2 = H$;
$R^1 = H$: $R^2 = Me$, Cl; $R^1 = Me$, $R^2 = H$

Attempts to employ this reaction to prepare the tellurium analogs of **99** failed.[131]

Other methods for the synthesis of **81** are of less preparative value, mostly because of the contamination of the **81** formed with a number of by-products.[132,133]

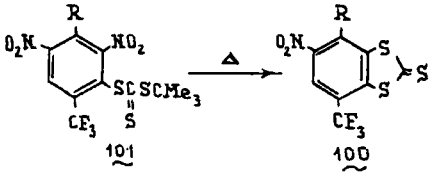


The usual way to convert an immonio function to a thione has been applied in the synthesis of 1,3-dithiole(selenole)-2-thiones;[1,2,4,6] the reaction of immonium salts with hydrogen sulfide is exemplified by the following reactions:[133]

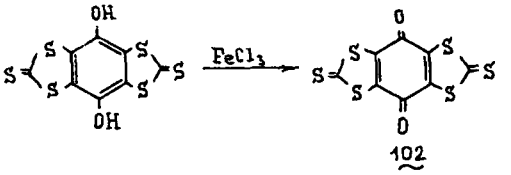


$R^1 + R^2 = (CH_2)_4$

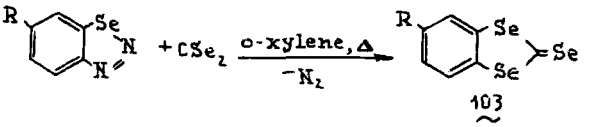
Some specific approaches to individual benzo-1,3-dithiole-2-thiones have been suggested. Thus, the nitro substituted compounds **100** have been prepared in 38–45% yield by reflux of acetic acid solutions of the *t*-butyl trithiocarbonates **101**[118] whereas **102** are formed from their dihydroxy precursors.[134]



R = H, Me_2N, NHPr

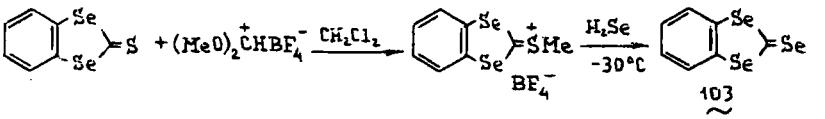


2.2.4.3. *Benzo-1,3-dichalcogenole-2-selones.* Apart from the synthesis of benzo-1,3-dithiole-2-selones **99** (X = Se) by reaction of the carbenes **37** with elemental selenium (see Section 2.2.4.2.),[131] two additional methods have been reported. By heating of benzo-1,2,3-selenadiazoles with carbon diselenide the selones **103** have been prepared in 60–70% yield.[31]

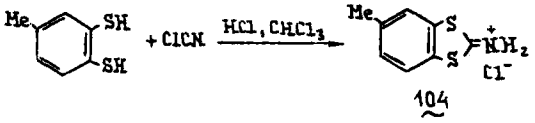


R = H, Me

Another route to the selone **103** (R = H) involves alkylation of the corresponding thione and subsequent treatment of the sulfonium salt formed with hydrogen selenide at −30 °C.[9]

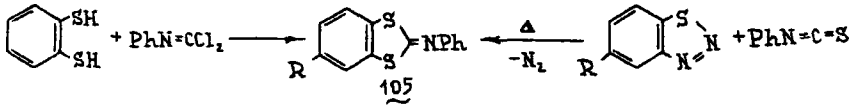


2.2.4.4. *2-Imino(immonio)-benzo-1,3-dithioles.* The main precursors for the title compounds are benzene-1,2-dithiols or dithiocarbamates. The 5-methyl derivative of the parent 2-imino-BDT **104** has been prepared in 87% yield by condensation of 4-methylbenzene-1,2-dithiol with ClCN.[135] Traces of ethanol were shown to catalyze the reaction.



104

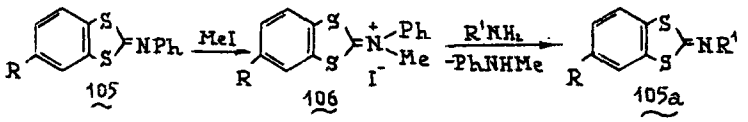
A general method for the synthesis of the 2-arylimino-BDT **105** is based on the addition of aryl isothiocyanates to thioketocarbenes **97**, generated by thermal decomposition of benzothiadiazoles.[127,136] However, the yields of **105** are rather low due to the parallel formation of thianthrenes.[136] The only example of the use of the phenylimino derivative of phosgene in the synthesis of 2-imino-BDT is its reaction with benzene-1,2-dithiol.[127]



105

R = H, Cl*, CF_3*, NO_2*, OCH_3*

For the exchange of the *N*-substituent of **105** the following sequence of reactions may be applied:[136]

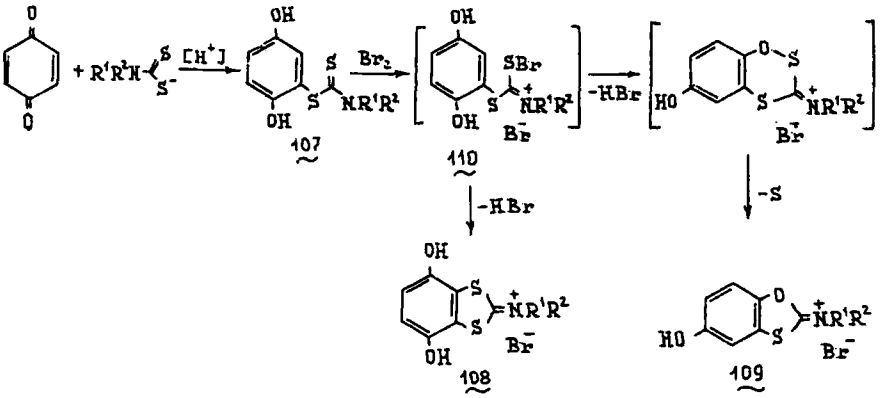


105 106 105a

R = H:
R^1 = $CH_2CH_2NMe_2$, OH, CH_2CO_2Et, $CH_2(CO_2Et)CH_2Ph$, NHPr-*n*, CH_2CH_2-indolyl-3, 2-thiazolyl and other cyclic amines;
R = H, Cl, CF_3, NO_2, OCH_3: R^1 = $NC(O)CH_2SC(O)$

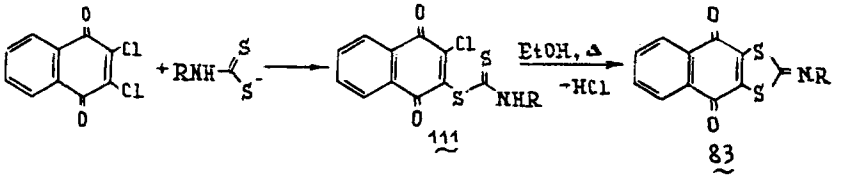
The most important method for the preparation of 2-imino-BDT containing hydroxy substituents on the benzene ring is the addition of dithiocarbamates to one of the double bonds of *p*-benzoquinone.[132] The reaction occurs most readily when an acetic acid solution of benzoquinone is added slowly to a solution of the dithiocarbamate in aqueous DMF. The adducts **107** may be isolated (in yields of 52–90%). Bromination of **107** leads, depending on the solvent, to either BDTs **108** (chloroform) or benzo-1,3-oxathioles **109** (methanol). The intermediacy of sulfenyl bromides **110** has been suggested.[132]

*The compounds were isolated as the immonio derivatives **106**[136]

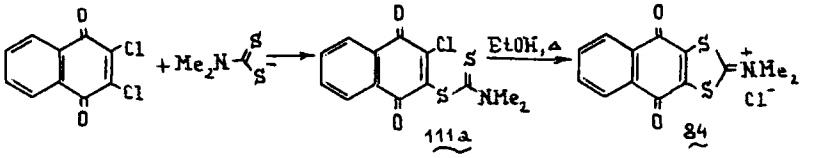


$R^1 = R^2 = Me$; $R^1 + R^2 = (CH_2)_4$; $R^1 = H$, $R^2 = i\text{-Pr}$

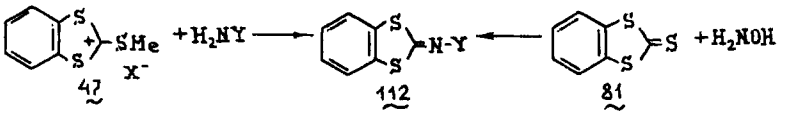
The formation of a benzodithiole ring by attachment of a dithiocarbamate moiety to a double bond of a quinone can also be achieved by nucleophilic substitution of halogens attached to that bond.[114,137] The reaction of 2,3-dichloronaphthoquinone with dithiocarbamates can serve as an example.[114]



R = Me, Et



By reaction of the 2-(methylthio)benzo-1,3-dithiolylium salts **47**[138,139] or the benzo-1,3-dithiole-2-thione **81**[44] with hydrazines or hydroxylamine, respectively, a number of compounds **112** has been prepared.



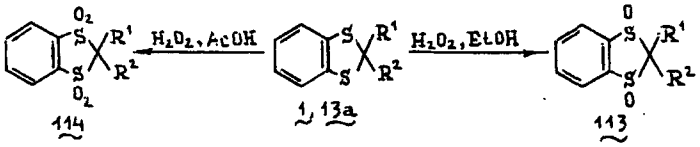
Y = NH_2, NHTos

3. REACTIONS OF BENZO-1,3-DICHALCOGENOLES

Electrophilic substitution reactions on the benzene ring of BDC have been studied rather infrequently. Nitration of benzo-1,3-dithiole-2-one affords 5-nitrobenzo-1,3-dithiole-2-one,[44,116,118] while the benzo-1,3-dithiole-2-thione a complex mixture of unidentified compounds was obtained.[118] Reactions of BDCS involving the chalcogen and carbon centers of the heterocycle have been studied in greater detail.

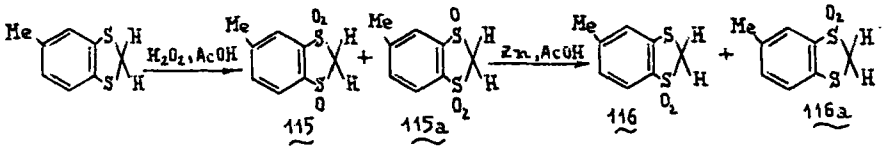
3.1 *Reactions of Benzo-1,3-dithioles at Sulfur Centers*

Benzo-1,3-dithioles, like acyclic sulfides, are susceptible to oxidation, depending on the reaction conditions, to either disulfoxides[62] or disulfones.[29,62] In some cases the reaction can be controlled by the choice of solvent. Thus, by oxidation of BDTs **1**, **13a** with 30% H_2O_2 in aqueous ethanol the disulfoxides **113** were obtained[62] whereas use of acetic acid as solvent leads to high yields of the disulfones **114**.[29,62]

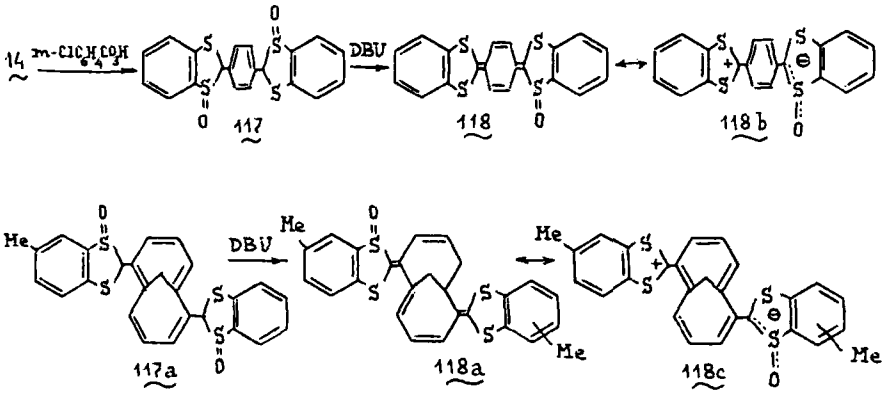


113 R^1 = α-C_4H_3S, R^2 = CH_2COMe
114 R^1 = R^2 = H; R^1 = H, R^2 = CH_2COPh, $CH_2COC_4H_3S$-α;
R^1 = α-C_4H_3S, R^2 = CH_2COMe

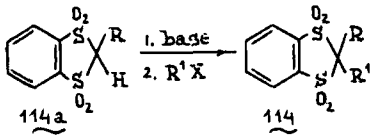
In the case of 5-methyl-BDT oxidation with hydrogen peroxide in acetic acid gives rise to a mixture of the two possible sulfoxide sulfones **115** and **115a**, which are transformed to the sulfones **116** and **116a** by reduction with zinc dust.[140]



m-Chloroperbenzoic acid has been employed in the oxidation of bis(benzo-1,3-dithiolyl-2) derivatives of **14** and **15** to give the disulfoxides **117** and **117a** in moderate yields.[51,141] A partial reduction of **117** and **117a** with DBU leads to the sulfoxides **118** and **118a** whose peculiar properties (inertness towards reducing agents such as dithionite, silanes, thiols, phosphines, and phosphites as well as a deep color[142]) are consequences of the substantial contribution of the polar resonance forms **118b** and **118c** to the ground state electronic structures of these molecules.

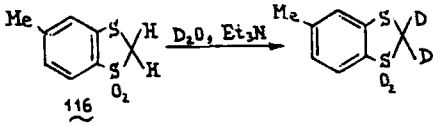


Due to the presence of two powerful electron-withdrawing groups in the disulfones **114** ($R^1 = R^2 = H$, $R^1 = H$, $R^2 = Alk$) they behave as rather strong CH-acids prone to mono- and dialkylation at the C(2) center under basic conditions (K_2CO_3 in DMF; NaH in THF or DMF).[29] In contrast to their acyclic analog bis(phenylsulfonyl)methane the disulfones **114** undergo dialkylation even upon treatment with sterically crowded alkyl halides. The yields of alkylated disulfones are in the range of 75–97%.[29]

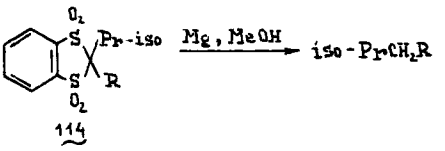


R = H: R^1 = *i*-Pr, $PhCH_2CH_2$; R = *i*-Pr:
R^1 = Me, Et, *i*-Pr, *i*-Bu, *cyclo*-$C_6H_{11}CH_2$, $PhCH_2CH_2$; R = $PhCH_2CH_2$:
R^1 = *i*-Pr, Me_3CCH_2

The single sulfonyl group in **116** suffices for rapid exchange of the methylene hydrogens for deuterium upon treatment of its 1,2-dimethoxyethane solution with D_2O in the presence of triethylamine.[140]



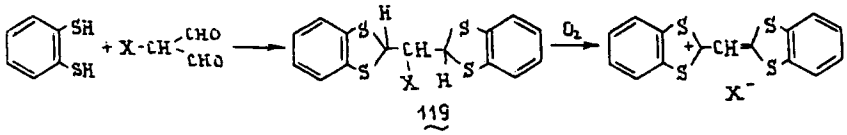
In order to remove the sulfonyl groups of the benzo-1,3-dithiole-1,1,3,3-tetraoxides **114** the latter are treated with magnesium in methanol solution.[29] The reaction is considered as a new useful approach to the synthesis of certain saturated hydrocarbons. The yields reach 50–72%, but the details of the reaction remain unclear.



R = $PhCH_2$, *cyclo*-$C_6H_{11}CH_2$

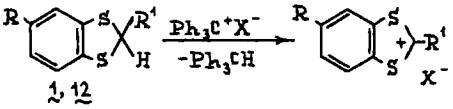
3.2 *Conversion of Benzo-1,3-dichalcogenoles to Benzo-1,3-dichalcogenolylium Salts*

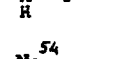
BDTS **1** and **12**, particularly those containing electron releasing groups, such as *p*-$Me_2NC_6H_4$[46,143] and *p*-$Me_2NC_6H_4CH=CH$,[46,143] are readily oxidized to the corresponding benzo-1,3-dithiolylium salts **6** by hydrogen peroxide, *p*-benzoquinone,[143] 2,3-dichloro-5,6-dicyano-*p*-benzoquinone,[52,54] *N*-chlorosuccinimide,[51] and even by air oxygen.[46,143] Illustrative is the transformation of BDT **119** to a monomethine dye when oxygen is bubbled through its chloroform solution.[46]

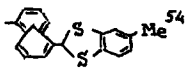


X = Cl, Br

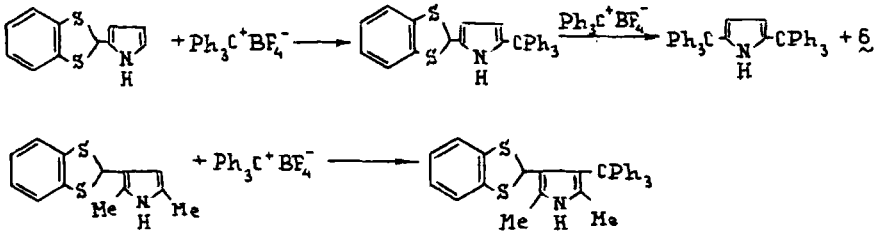
Another way of conversion of BDTS to dithiolylium salts is hydride ion abstraction by the triphenylmethyl cation in the shape of $Ph_3C^+BF_4^-$,[38,39,50,53,54,56,66,67,88] $Ph_3C^+ClO_4^-$,[16,17,21] or $Ph_3C^+SbCl_6^-$.[51,54,56] The preferred solvents in this reaction are acetonitrile and, when the hexachloroantimonate is employed, methylene chloride.



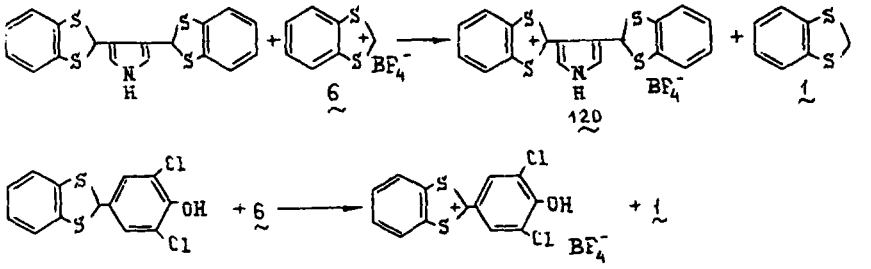
R = H: X = BF_4^-:
R^1 = H,[37,38], indolyl-3, 2-methylindolyl-3, *N*-methyl-indolyl-3;[66]
Ph,[88] 4-CH_3O-C_6H_4;[88] X = ClO_4^-: R^1 = D,[21] Ph;[16,17]
4-$MeOC_6H_4$,[16] 4-ClC_6H_4,[16] *cyclo*-C_6H_{11},[16,54]  ;[67]

R = Me, X = BF_4^-, R^1 =  [54]

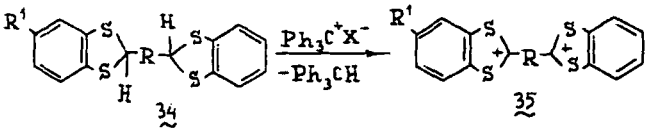
Peculiar in this reaction is the behavior of BDTs containing a 2-pyrrolyl moiety.[67]



Benzo-1,3-dithiolylium tetrafluoroborate **6** has also been used as the hydride ion abstracting agent.[64,67,66] The advantage of its use instead of triphenylmethyl tetrafluoroborate is that the product **120** is obtained in higher yield (76%) and without any contamination.[67]

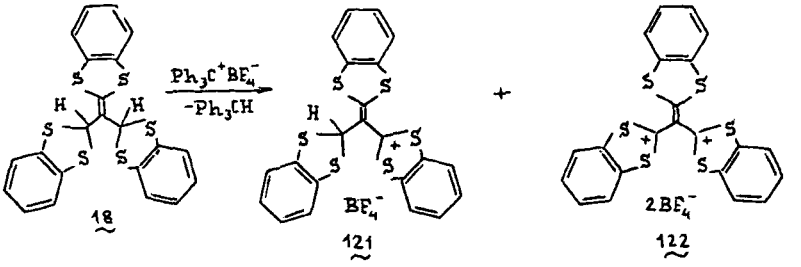


Bis(benzo-1,3-dithiolylium) salts **35** have been obtained in a similar way.[50,53,55-57,88]



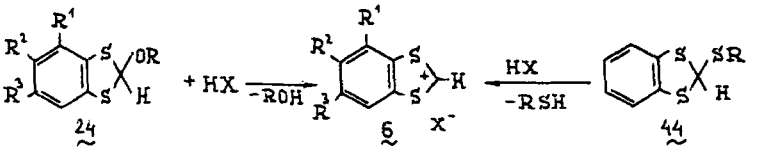
R^1 = H: X = BF_4^-: R = *p*-C_6H_4,[50,88] *m*-C_6H_4,[50] 4-$C_{10}H_6$;[53] R = CH_2CH_2.
X = BF_4^-,[56] $SbCl_6^-$;[55,57] R = 2,5-$(Me_2N)_2C_6H_2$: X = BF_4^-[50]

It is worth noting that in contrast to its *m*- and *p*-isomer *o*-bis(benzo-1,3-dithiolyl-2)benzene cannot be converted to a bis(dithiolylium) salt by treatment with $Ph_3C^+BF_4^-$; not even when this is in excess.[50] The dithiole **18** reacts with $Ph_3C^+BF_4^-$ to a mixture of the mono- and bis(dithiolylium) salts **121** and **122**.[58]



Benzo-1,3-dithiolylium salts **6** are also formed in reactions of 2-alkoxy-BDT **24**[17,37,38,75,76] and 2-alkylthio-BDT[37,38] with strong acids such as HBF_4,[37,38,75,76] $HClO_4$[17,37] and HX (X = I, Br, Cl)[37] in acetic anhydride or diethyl ether solution. The yields of **6** are nearly quantitative. The reaction is totally inhibited when all four positions of the benzene ring of the 2-alkoxy-BDT are occupied by chlorine or bromine atoms.[76]

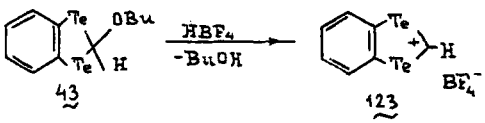
The first benzo-1,3-ditellurolylium salt, **123**, was prepared in 67% yield by coupling 2-butoxy-BDTe with HBF_4 in acetic anhydride solution.[43,80] It should be



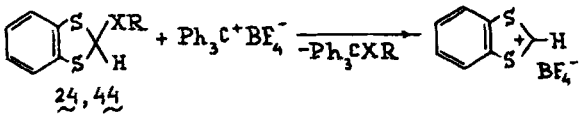
X = BF_4^-: R = *iso*-C_5H_{11}:
$R^1 = R^2 = R^3 = H$[37,38,75,76]
(the substitutents R ≠ H are indicated below)
R^1 = Me, R^2 = Me, Cl, I, NO_2;
$R^2 + R^3 = (CH{=}CH)_2$;[75]
$R^1 = R^2 = R^3 = H$: R = *iso*-C_5H_{11}:
X = ClO_4^-,[17,37] HSO_4^-,[37] I^-,[37] Br^-,[37] $ZnCl_3^-$;[37]
X = BF_4^-:
R = Me,[37,38] Et,[37] Pr,[37] Bu,[38] *iso*-Bu[37]

X = BF_4^-:
R = Et,[37,38] Ph,[37,38] *cyclo*-C_6H_{11}[37]

noted that attempts at the synthesis of 1,3-ditellurolylium salts based on the reaction of 1,3-ditelluroles with triphenylmethyl tetrafluoroborate in acetonitrile solution failed.[144] Instead of the expected 1,3-ditellurolylium salts rearrangement products, 1,2-ditellurolylium salts are formed which rapidly decompose with extrusion of elemental tellurium.



The triphenylmethyl cation in its reaction with 2-alkoxy-BDT **24** and 2-alkylthio-BDT in acetonitrile solution acts as an acceptor of RX^- (X = O, S) anions rather than of hydride ion.[79]

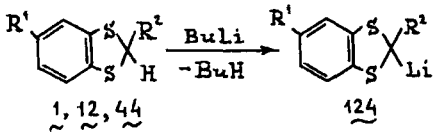


XR = MeO, *iso*-PrO, *iso*-$C_5H_{11}O$, EtS

On the other hand the corresponding reaction with 2-(*t*-butylthio)-BDT leads to benzo-1,3-dithiole-2-thione via hydride ion abstraction.[79]

3.3 *Metallation of Benzo-1,3-dithioles*

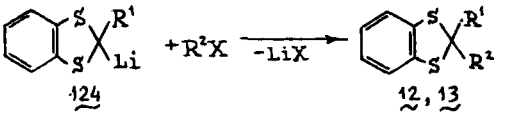
The BDTs **1**, **12**, and **44** readily undergo lithiation in the 2-position upon treatment with butyl-lithium in THF solution at low temperature.[18,19,27,32,71,93,145,146]



1, **12**, **44** **124**

R^1 = H: R^2 = H,[18,27,32,93,145,146] Me,[18] *n*-Pr,[18,19,27] *iso*-Pr,[18] *cyclo*-C_6H_{11},[19,27] SMe;[71,146]
R^2 = SMe: R^1 = H, Cl[71]

2-Lithio-BDTs are susceptible to a variety of reactions common for organolithium compounds: with D_2O,[32] alkyl halides,[18] aldehydes,[18] ketones,[18] trialkylboranes,[19,27] thiophosgene,[93] thiones,[71] and carbon disulfide,[145] the yields being invariably high. The reactions with trialkylboranes and thiones will be dealt with below (Section 3.4. and 4.). Here we shall consider those with alkyl halides[18,145] and with carbonyl compounds.[18] The former allow the most convenient introduction of an alkyl group in the 2-position of a BDT.[18,145]

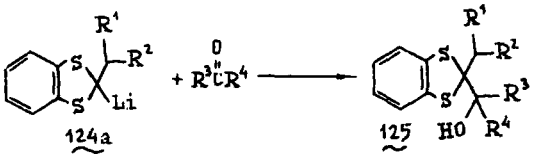


124 **12**, **13**

R^1 = H: R^2 = Me,[145] *n*-Pr;[18] R^1 = *n*-Pr: R^2 = Me,[18] *n*-Bu[18]

When reacting with carbonyl compounds and oxiranes the 2-lithio-BDTs **124** give the functionalized alcohols **125** in 67–94% yield.[18]

The compounds **125** proved to be useful synthons for the preparation of some sulfur-containing heterocycles not easily accessible by other methods. Thus, cou-

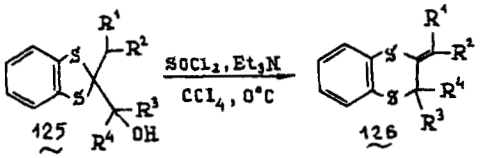


124a **125**

R^1 = R^2 = H: R^3 = H, R^4 = Et; R^3 + R^4 = *cyclo*-C_6H_8; R^1 = R^2 = Me: R^3 = H, R^4 = Ph; R^1 = Et: R^2 = H: R^3 = H: R^4 = Ph, Me, Me_2CHCH_2; R^3 + R^4 = *cyclo*-C_6H_{10}; R^3 = Me, R^4 = Ph

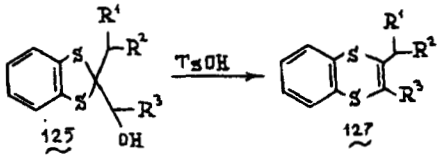
pling of **125** with $SOCl_2$ in the presence of triethylamine leads to a ring-expanding

reaction giving rise to 2-alkylidene-1,4-benzothiins **126** in 73–92% yield[147] (in the case of **126** ($R^1 = R^2 = R^4 = H$, $R^3 = Et$) the yield is only 14%). The reaction is highly regiospecific. Only one of two possible (provided $R^1 \neq R^2$) geometric (E,Z)-isomers is formed whose nature has not been proven, although the assignment of the (Z)-structure seems more plausible, at least in the case of compounds with $R^1 = H$.[147]



$R^4 = H$: $R^1 = R^2 = H$, $R^3 = Et$; $R^1 = R^2 = Me$, $R^3 = Ph$; $R^1 = Et$, $R^2 = H$: $R^3 = Me$: *i*-Bu; Ph; $R^1 = Et$, $R^2 = H$, $R^3 = Me$, $R^4 = Ph$;
$R^1 = Et$, $R^2 = H$, $R^3 + R^4 = (CH_2)_5$

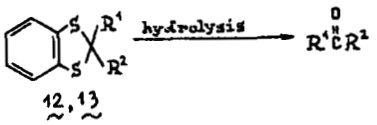
Upon treatment of BDTs **125** ($R^4 = H$) with acids (TsOH, CF_3COOH) isomers of **126**, i.e. the 1,4-benzodithiins **127** are obtained in high yields.[147]



$R^1 = R^2 = H$, $R^3 = Et$; $R^1 = R^2 = Me$, $R^3 = Ph$;
$R^1 = Et$, $R^2 = H$: $R^3 = Me$, *i*-Bu, Ph

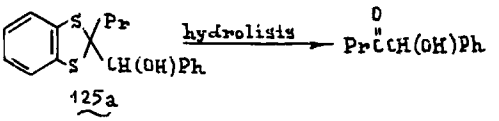
3.4 *Hydrolysis and Reduction of Benzo-1,3-dithioles*

BDTs can be regarded as cyclic thioketals or thioacetals. It is, therefore, obvious that their hydrolysis should lead to the corresponding ketones and aldehydes. The reaction is usually performed by refluxing aqueous THF solutions of **12** or **13** containing catalysts such as HgO and $HgCl_2$,[15] chloramine T/Hg^{2+},[16,17] HgO/$BF_3 \cdot OEt_2$,[18,22,24,25] and HgO/HBF_4,[20,21,23] the latter being the most efficient.

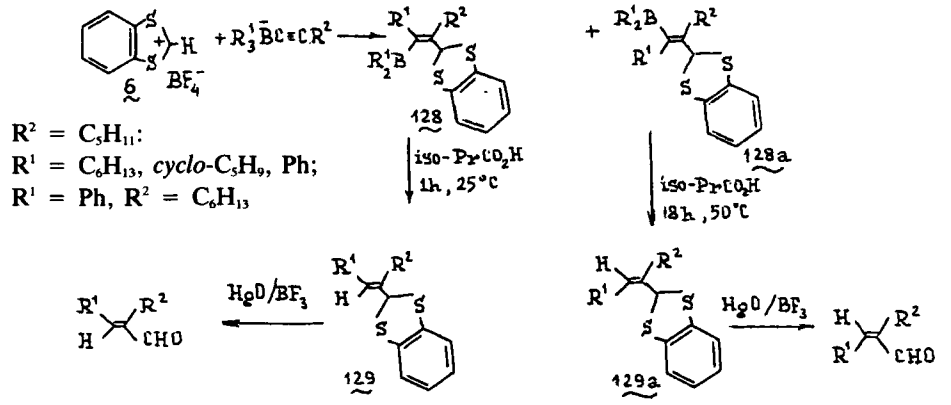


$R^1 = H$:
R^2 = 4-$Me_2NC_6H_4$,[15] 2-Me-4-$(Me_2N)C_6H_3$,[15] 4-$(Me_2N)C_{10}H_7$,[15] Ph,[17,20] 4-$MeOC_6H_4$,[17,20] 4-ClC_6H_4,[20] *n*-C_9H_{19},[20] *n*-$C_{15}H_{31}$,[20] $(CH_2)_{10}CHO$,[20] PhCH = CH,[20] Pr,[17,18] *cyclo*-C_6H_{11},[17,23] *cyclo*-C_6H_{10}(3-*t*-C_4H_9),[23] *cyclo*-$C_{12}H_{25}$,[23] CH_2Bu-*t*,[23] $CH_2C_8H_{17}$,[23] CH_2Ph,[23] $CH(Me)C_6H_{11}$-*cyclo*,[23] $CH(Me)C_8H_{17}$-*n*,[23] $CH(PhCH_2)_2$,[23] $CH(C_6H_{13})_2$;[23]
$R^1 = Pr$, $R^2 = Bu$,[18] $R^1 = R^2 = Ph$;[17,20] $R^1 = Me$: $R^2 = Ph$;[17,20] *n*-C_8H_{17};[20] $R^1 = OEt$, $R^2 = Ph$;[20] $R^1 + R^2 = (CH_2)_2CH(t\text{-Bu})CH_2$[20]

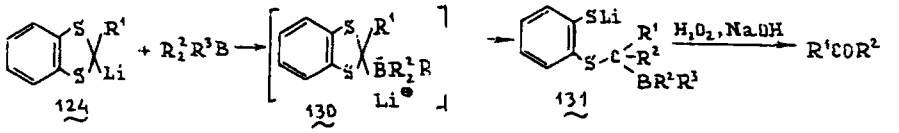
By hydrolysis of the BDTs **125a** (for their preparation see Section 3.3.) α-hydroxy ketones have been obtained.[18]



A novel stereospecific synthesis of α,β-unsaturated aldehydes has recently been reported. Benzo-1,3-dithiolylium salts **6**[22] and 2-lithio-BDTs **124**[19] serve as the starting materials. Upon treatment with lithium trialkylalkynylborates **6** afford a mixture of the geometric isomers **128** and **128a** in yields higher than 70% which, in turn, can be selectively converted to derivatives of 2-vinyl-BDTs **129** and **129a** by reaction with *i*-PrCOOH.[22] Hydrolysis of **129** and **129a** in the presence of HgO/BF_3 gives rise to the easily separable (Z)- and (E)-isomers of α,β-unsaturated aldehydes.



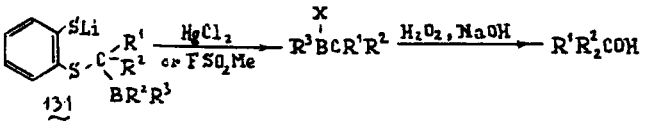
A convenient ketone synthesis is based on the reaction of trialkylboranes with 2-lithio-2-alkyl-BDTs **124**.[19] An initial adduct **130** is formed which undergoes intramolecular rearrangement by B→C migration of one of the alkyl groups. The resulting thiolate **131** is readily oxidized by hydrogen peroxide in basic media to afford a ketone in 69–93% yield.[19] Many trialkylboranes, even those with bulky alkyl groups, will participate in this reaction.



R^1 = *cyclo*-C_6H_{13}, *n*-Pr; R^2 = R^3 = *n*-C_6H_{13}; R^2 = *cyclo*-C_6H_{13}, R^3 = *n*-C_8H_{17}; R^2 + R^3 = *cyclo*-C_5H_{10}, *cyclo*-C_6H_{12}, *exo*-norbornyl

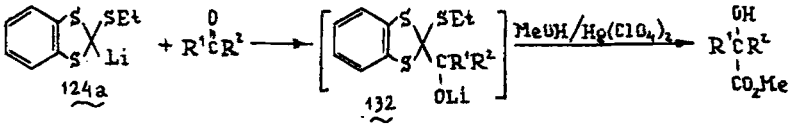
The reaction can be directed to give tertiary alcohols provided the interme-

diates **131** are treated with either $HgCl_2$ or methyl fluorosulfonate. Such a treatment brings about the B→C migration of the second alkyl group and after oxidation leads to a tertiary alcohol.[27]



R^1 = *cyclo*-$C_{16}H_{13}$, *n*-Pr; R^2 = R^3 = *n*-C_6H_{13}, *n*-C_8H_{17};
R^2 + R^3 = *cyclo*-C_6H_{13}, norbornyl

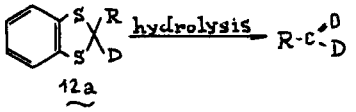
2-Lithio-2-(ethylthio)-BDT reacts with ketones with the formation of **132** whose methanolysis in the presence of mercury(II) perchlorate gives α-hydroxy esters in high yields.[26]



R^1 = Ph: R^2= Me, 4-$CH_3C_6H_4$; R^1 = R^2 = Ph; R^1 + R^2 = 

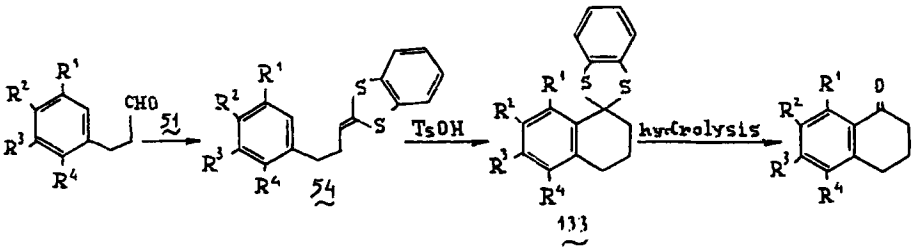
When xanthone is used in this reaction the adduct **132** is isolable in quantitative yield (96%). However, in this particular case its hydrolysis leads to a mixture of the starting xanthone and the methoxy ester.

A very convenient method of preparation of aldehydes-d_1 is based on the hydrolysis of 2-R-BDTs **12a** deuterated in the 2-position.[16,21] Considering that compounds **12a** are easily accessible by either high yield reduction of 2-R-benzo-1,3-dithiolylium salts with $NaBD_4$ or $LiAlD_4$[16] or by coupling of benzo-1,3-dithiolylium salts deuterated in the 2-position with organomagnesium compounds[21] (see Section 2.1.2.2.), this method seems to have a wide scope of application.

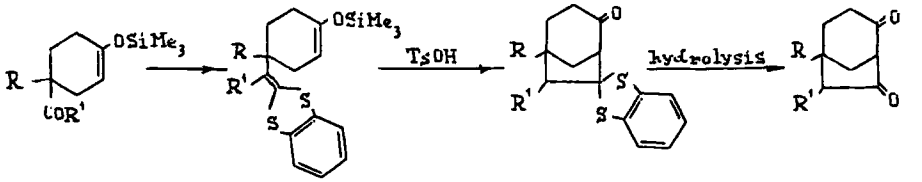


R = Ph,[16,21] 4-$MeOC_6H_4$,[16,21] 4-ClC_6H_4,[16] *cyclo*-C_6H_{11},[16] *n*-C_9H_{19}[16,21]

Recently an efficient method was developed for the preparation of carbocyclic compounds, some of them closely resembling natural products, involving BDT derivatives as starting compounds.[24,25] The method is illustrated by a synthesis of tetralones. Dithiafulvenes **54** (R^1-R^4 = OAlk) obtained by standard procedures (see Section 2.2.3.) were cyclized to the spiranes **133** in 56–77% yield. Hydrolysis of **133** in aqueous THF containing $HgO/BF_3 \cdot Et_2O$ affords tetralones in 55–62% yield.[24,25]

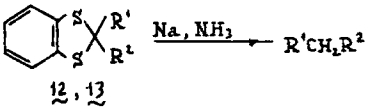


In a similar way bicyclo[3.2.1]octanediones were prepared as shown below. Other examples of the preparation of cyclic ketones are to be found in the literature.[25]

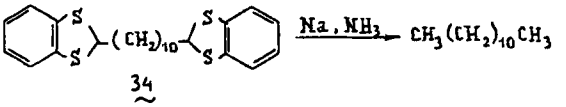


At the same time other preparative possibilities involving the hydrolysis of BDTs still remain unexplored. Thus, by hydrolysis of **13a** and **30** 1,3-diketones and diketoaldehydes could be obtained. Also promising seems the possibility of involvement of BDTe in similar transformations. The greater lability of C-Te bonds as compared to C-S bonds warrants milder conditions for such hydrolyses.

It has already been noted that by reaction of 2,2-disubstituted benzo-1,3-dithiole 1,1,3,3-tetraoxides **116** with magnesium in methanol saturated hydrocarbons may be obtained in high yields.[29] These may be also prepared by reductive cleavage of the C-S bonds of the BDTs **12** and **13** by treatment with sodium in liquid ammonia.[28] The yields are in the range 50–93%.



R^1 = H: R^2 = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, $PhCH_2$, *n*-C_9H_{19};
R^1 = Me: R^2 = Ph, *n*-C_8H_{17}; R^1 = R^2 = Ph



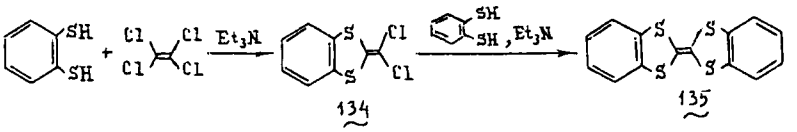
Considering that the starting materials for the immediate precursors of the BDTs, the benzo-1,3-dithiolylium salts, are carboxyl acids, aldehydes, and

ketones, the above-mentioned reactions amount to a reduction of carbonyl-containing compounds to hydrocarbons.[28]

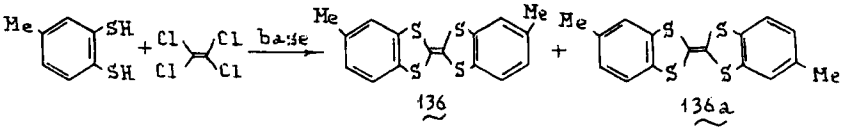
4. SYNTHESIS OF DIBENZOTETRACHALCOGENAFULVALENES

4.1 *Reactions of Benzene-1,2-dichalcogenols with Tetrachloroethylene*

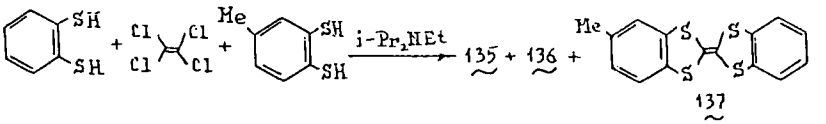
The first representative of DBTCF, dibenzotetrathiafulvalene DBTTF, was prepared by coupling of benzene-1,2-dithiol with tetrachloroethylene (TCE) under basic conditions.[8] The synthesis can be carried out in two steps. Reaction of benzene-1,2-dithiol with excess TCE in the presence of triethylamine in DMF solution at room temperature affords 2-dichloromethylene-4,5-benzo-1,3-dithiole **134** as the main product, the yield amounting to 59%.[148] At this step DBTTF represents a by-product (the yield is 5%). When the dithiole **134** is treated with benzene-1,2-dithiol in boiling MeCN in the presence of triethylamine DBTTF is formed in high yield.[148]



In a similar way bis(5-methylbenzo-1,3-dithiolylidene-2) **136** has been synthesized.[149] When $(i\text{-Pr})_2\text{EtN}$ was used as the base the yield of **136** amounted to 33%. In the case of the less basic reagent pyridine the yield of **136** is only 15%. Most probably, reaction product **136** is actually a mixture of two isomers.

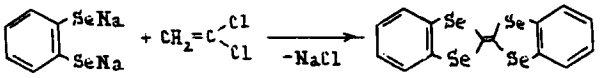


A similar reaction has been used for the synthesis of the unsymmetric DBTTF 5-methyl-bis(benzo-1,3-dithiolylidene-2), **137**.[149] Even though the reaction mixture contained appreciable amounts of the symmetric DBTTFs **135** and **136**, compound **137** was readily isolated by crystallization from the pyridine solution. The yield of pure **137** was 10–13%.



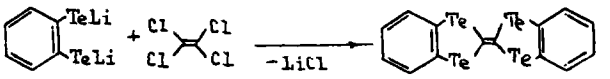
Dibenzotetraselenafulvalene (DBTSeF) **138** has been prepared in 48% yield by reaction of disodium benzene-1,2-diselenolate with 1,1-dichloroethylene.[126]

The reaction is assumed to involve the formation of an acetylenic intermediate.



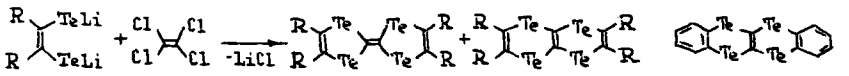
138

The synthesis of the last member of the series of DBTCFs, dibenzotetratellurafulvalene (DBTTeF) **139**, in only 10% yield has been achieved by coupling of dilithium benzene-1,2-ditellurolate with TCE.[10,150]



139

However, vis-a-vis the fact, discovered in the course of a detailed examination of the synthesis of tetratellurafulvalenes (TTeF),[151–157] that reaction of ethene-1,2-ditellurolates with TCE or tetrabromoethylene also leads, along with TTeF, to the isomeric six-membered heterocyclic compounds—derivatives of 1,4,5,8-tetratelluranaphthalene,[141] the possibility of a contamination of **139** with a substantial amount of dibenzotetratelluranaphthalene **142** cannot be ruled out.



140 141 142

R = H,[154,155] $(CH_2)_3$,[151–153] $CH_2CMe_2CH_2$,[156] $CH_2CH(Me)CH_2$,[157] CH_2-C(cyclo-C_3H_4)-CH_2[156]

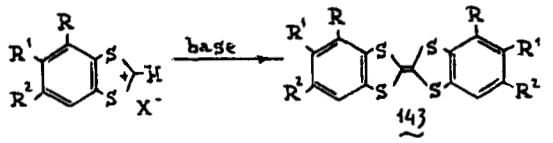
This means that reactions based on the use of TCE provide no unambiguous route to TTeF and its benzoannelated derivatives and that the development of alternative methods involving synthons with preformed 1,3-ditellurole fragments is gaining importance.

4.2 *Synthesis of Dibenzotetrachalcogenafulvalenes via Benzo-1,3-dichalcogenole-2-carbenes*

The dimerization of the appropriate cyclic carbenes **37** is one of the most useful methods of synthesis of symmetric DBTTFs. Several ways to generate these carbenes are known: deprotonation of benzo-1,3-dithiolylium cations, cycloaddition of carbon disulfide to dehydrobenzene, thermal decomposition of 2-alkoxy-BDT **24**, and the Bamford-Stevens reaction.

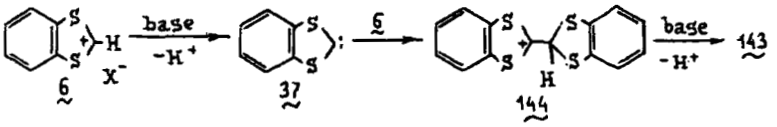
4.2.1. *Deprotonation of benzo-1,3-dithiolylium cations.* A series of DBTTFs has been obtained by treatment of perchlorates or tetrafluoroborates of benzo-1,3-

dithiolylium **6** and its congeners with various bases, Et_3N,[37,38,75,82,120,158–160] $(i\text{-Pr})_2EtN$,[139,160] Pr_3N,[37] DBU,[75] and DMF.[37,75]

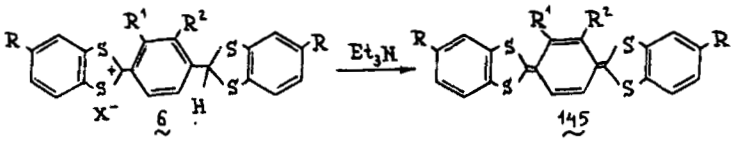


R = R^1 = R^2 = H[37,38,75,82,140,158,160] (46–93%); R = R^2 = H:
R^1 = Me[75,139] (44–67%), Cl[75,158] (55–88%), I[75] (95%), NO_2[75] (60%),
OMe[120] (30%), OEt[120] (29%);
R = H: R^1 + R^2 = $(CH{=}CH)_2$[75] (88–99%), R^1 = Cl, R^2 = Me[158] (79%);
R^2 = H: R^1 + R^2 = $(CH{=}CH)_2$[159] (40%); R = Me:
R^1 = R^2 = H[75] (67–94%)

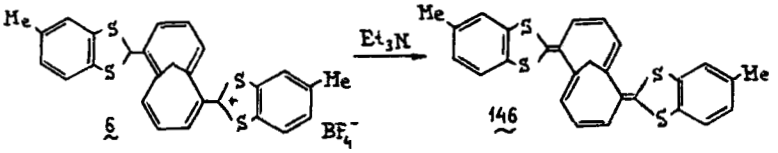
A plausible reaction mechanism is shown below featuring the intermediate cation **144**.[37,82]

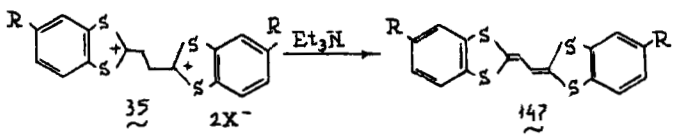


The deprotonation of benzo-1,3-dithiolylium salts **6**[52,53,161] and **35**[55–57] with triethylamine has been utilized for the preparation of a variety of derivatives of BDTTF **145–147**.



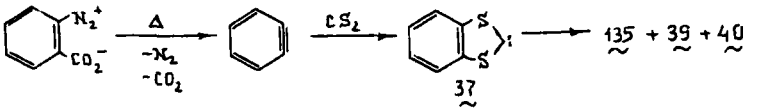
X = $SbCl_6^-$, ClO_4^-: R = R^1 = R^2 = Me (~100%);[52]
X = BF_4^-: R = H, R^1 + R^2 = $(CH{=}CH)_2$[53]



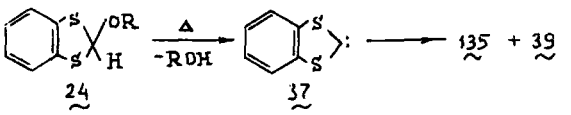


X = BF_4^-; R = H (48%),[56] Me (57%)[56]; X = $SbCl_6^-$: R = H (80%)[55,57]

4.2.2. *Other approaches to benzo-1,3-dithiole-2-carbenes.* Thermolysis of 2-diazoniobenzenecarboxylate in aprotic solvents is a convenient way to dehydrobenzene which readily reacts with carbon disulfide to form the carbene **37** dimerizing to DBTTF.[73,131,162] Small amounts of 2,2'-spiro-bis(benzo-1,3-dithiole) **39** and 2,2'-(*o*-phenylenedithio)-bis(benzo-1,3-dithiole) **40** are also formed in this reaction due to the presence of trace amounts of water in the reaction mixture. The reaction scheme is similar to that discussed in Section 2.2.1., water acting as a weak acid.



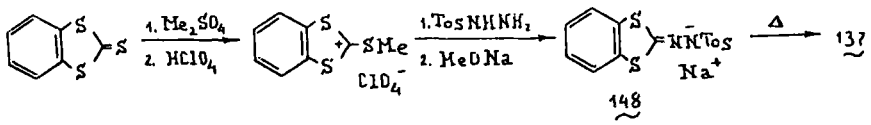
By thermolysis of 2-alkoxy-BDT **24**, usually carried out in triglyme,[163] acetic anhydride,[163,164] pyridine,[164] or without solvent[163] by heating **24** at 200 °C, DBTTFs have been prepared in 10–55% yield.[163,164] Spiran **39** was found to be an invariable by-product of this reaction. Fortunately, however, it may be easily separated from DBTTF by simply washing the reaction mixture with a small amount of benzene.



R = Me, Bu, *i*-C_5H_{11}, *n*-C_6H_{13}

Due to the ready accessibility of 2-alkoxy-BDTs and the simplicity of their transformation to DBTTFs, the above procedure is considered to be the most convenient way to the latter compounds.

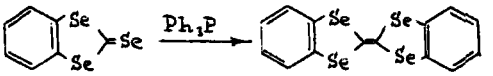
The Bamford-Stevens reaction should also be mentioned among the other procedures. A typical example is the thermolysis of sodium tosylhydrazonate **148** in diglyme solution, DBTTF being formed in 51%.[139] The carbene mechanism follows from the fact that 2-benzyloxy-BDT **24** (R = OCH_2Ph) was isolated in 38% yield when the thermolysis was carried out in benzyl alcohol solution.



4.3 *From Benzo-1,3-dichalcogenole-2-ones (-thiones, -selones)*

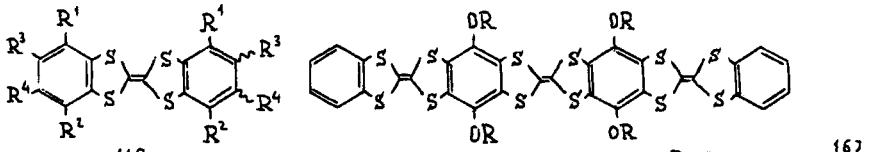
A general method of synthesis of various tetrachalcogenafulvalenes (TCF) is based on assembling the molecular framework from two 1,3-dichalcogenylidene moieties, the source for which is the reaction of a 2-oxo(-thio, -seleno)-1,3-

dithiole with a P(III) compound. In the DBTCF series this reaction was successfully applied to the synthesis of DBTSF **138** which was obtained in 60% yield from **103**.[9,31]



103 **138**

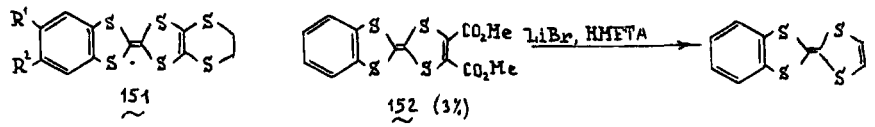
Similar reactions involving diverse 2-oxo[111,113] and 2-thio derivatives[122,160,165–167] of BDTs and trimethyl or triethyl phosphite were used in the preparation of a variety of DBTTFs.



149 **150** R = Et, n-$C_{16}H_{13}$[167]

$R^1 = R^2 = R^4 = H$: R^3 = H (51%)[160,165] Me (25–50%);[160,166] $R^1 = R^2$ = H: $R^3 = R^4$ = Me (68%),[166] SMe (45%)[111] $R^3 + R^4$ = SC(O)S (96%),[111] $S(CH_2)_2S$ (73%),[111] SC(S)S (42%);[122]
$R^3 + R^4$ = SC(O)S: $R^1 = R^2$ = SMe (96%),[113] SC_5H_{11} (86%);[113]
$R^3 + R^4$ = $(CH=CH)_2$: $R^1 = R^2$ = OMe (30–90%),[165] OCOMe (30–90%).[165]

The coupling of two different BDT-2-thiones by abstraction of thione sulfur with phosphites is a widely employed method of preparation of the nonsymmetrical DBTTFs **151**[166] and **152**.[168] A mixture of products from such a reaction could be separated by chromatography.



151 **152** (3%)

$R^1 = R^2$ = H (14%), Me (5%); R^1 = H, R^2 = Me (2%)

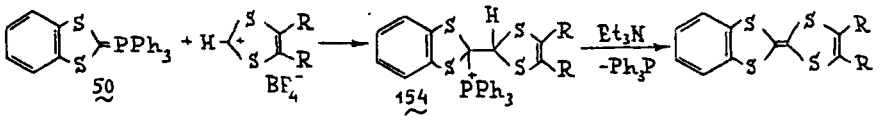
It has been usually assumed that the reaction of phosphines and phosphites with BDT-2-thiones produces the carbenes **37** in one step. However, a recent finding[169] indicates that the carbenes are formed via the adducts **153**.

153

4.4 *Reactions of Phosphoranes with Benzo-1,3-dithiolylium Salts*

It should be stressed that because of low yields and contamination of the target compound with by-products the above-mentioned reactions are of limited use for

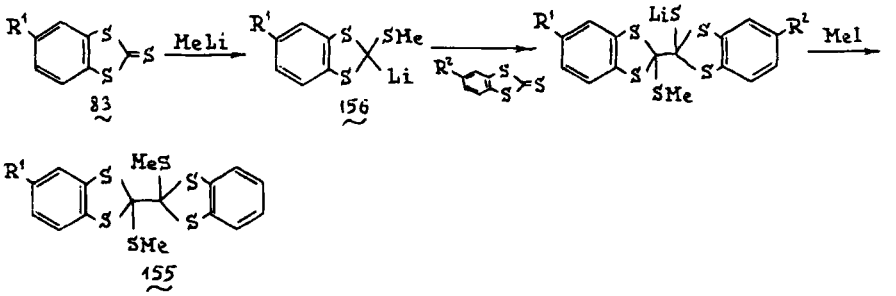
the preparation of nonsymmetric DBTCFs, i.e. those with nonidentical BDC-ylidene moieties. In 1978 a method was developed which allowed to overcome the drawbacks inherent in the non-selective approaches.[92] This method is based on the reaction of phosphoranes **50** with 1,3-dithiolylium salts implying the following sequence of reactions.



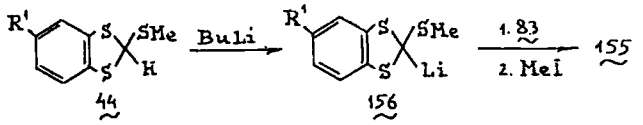
R = H[92,171] (40%), Me[92,171] (30%), R + R = $(CH_2)_3$[171] $(CH_2)_4$[92,171] (31%)

4.5 *Thermal Decomposition of Hexathioorthooxalates*

This reaction[71,172] may be regarded as a general way to nonsymmetrical DBTTFs, preferable to those described above when nonsymmetrical DBTTFs are to be prepared. Two slightly different procedures have been suggested for the preparation of the starting **155**.[71,172] The first one involves addition of methyllithium to BDT-2-thione **83** and subsequent treatment of the adduct **156** with an additional amount of **83**.[71] The yields of symmetrical hexathioorthooxalates are rather good, but the approach to nonsymmetrical DBTTF suffers from the same shortcomings which were mentioned in Section 4.3.

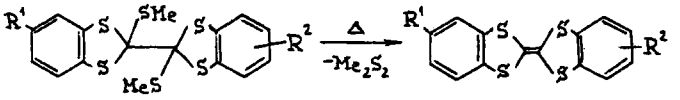


In this connection an improvement of the method has been suggested consisting of the preparation of **156** through deprotonation of 2-(alkylthio)-BDT **44** with butyllithium.[71] In this way interaction of the anion **156** with the parent BDT-2-thione **83** leading to symmetrical **157** may be avoided. Treatment of **156** with another equivalent of a structurally different BDT-2-thione results in the formation of the non-symmetrical hexaorthothiooxalate **155** ($R^1 \neq R^2$), virtually uncontaminated with its symmetrical counterpart **157** ($R^1 = R^2$).



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

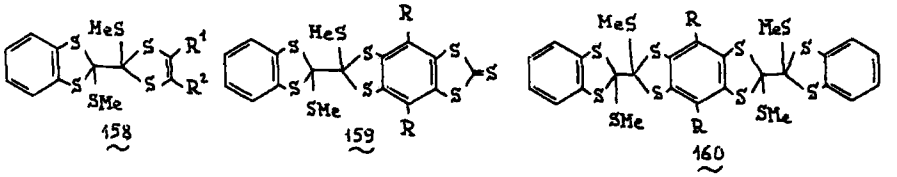
Thermolysis of **155** occurs smoothly in boiling CCl_4, tetrachloroethane, or toluene to afford DBTTF in 75–95% yield.[172] An acceleration of the reaction can be achieved by addition of catalytic amounts of TsOH.[172]



155

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

The hexathioorthooxalates **158–160** readily undergo thermal decomposition under these conditions.[167,172,173]



158 **159** **160**

R^1 = H, Me; R^2 = Me; $R^1 + R^2 = (CH_2)_3$[172]

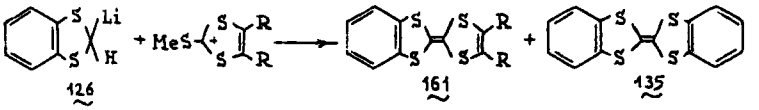
R = OEt,[167] OC_6H_{13}[167]

R = 3,5-di-*t*-Bu-$C_6H_3CH_2O$,[173] OEt[167]

4.6 *Other Methods*

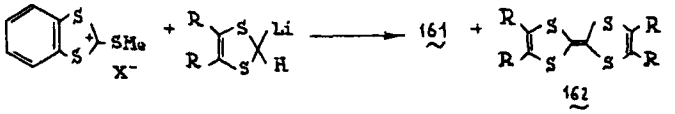
Other methods of preparation of DBTTFs, as a rule, are represented by single examples and are not of broad synthetical application.

The reaction of 2-lithio-BDT **124** with 2-(methylthio)-1,3-dithiolylium salts **146** was conceived to be a method of preparation of nonsymmetrical DBTTFs but turned out to suffer from the same shortcomings, i.e. side formation of symmetrical DBTTF like in the other reactions considered in Sections 4.1.-4.5



126 **161** **135**

R = Me, R + R = $(CH{=}CH)_2$

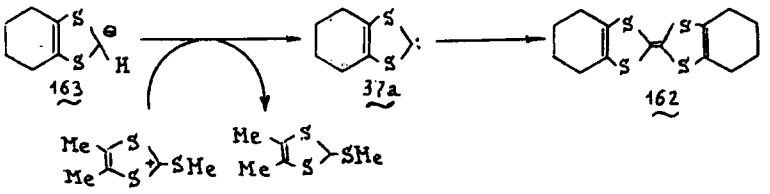


161 **162**

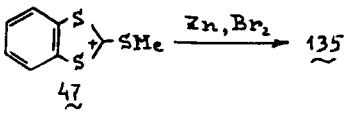
R + R = $(CH{=}CH)_2$, $(CH_2)_4$

The formation of the symmetrical TTFs **135** and **162** was thought to take place by dimerisation of the cyclic carbenes **37a** formed by abstraction of a hydride

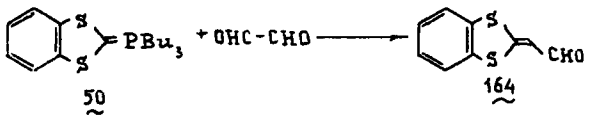
ion from the corresponding carbanion. This was proven by the fact that 2-(methylthio)-1,3-dithiol was found among the products of the reaction of 2-(methylthio)-1,3-dithiolylium cation with 2-lithio-TTF **163**.[146]



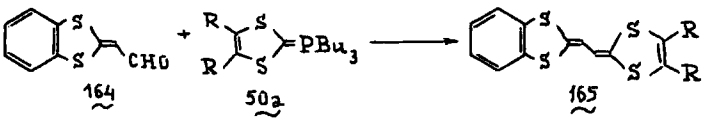
As is known to be the case with tetrathiafulvalenes,[2,6] DBTTF may be prepared from 2-(methylthiobenzo)-1,3-dithiolylium salt **47** by treatment with zinc dust in the presence of oxidants such as Br_2, I_2, and some others.[174] The yield of DBTFF is about 30%.



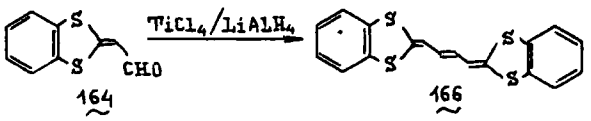
Methods of synthesis of vinylogs of DBTTF have been described, carbaldehyde **164** being employed as the starting material.[94]



By reaction of **164** with the phosphoranes **50a** the compounds **165** have been obtained in good yield.[94] Further elongation of the conjugated chain by going on from **165** to **166** was achieved by reductive coupling of **164** with the $TiCl_4$/$LiAlH_4$ system.[95]



R = CO_2Me, R + R = $(CH{=}CH)_2$



5. OUTLOOK

In conclusion, some general observations concerning the development of the chemistry of benzo-1,3-dichalcogenoles merit consideration.

1. The synthesis and transformations of benzo-1,3-dithioles have been studied in much more detail than those of benzo-1,3-diselenoles and benzo-1,3-ditelluroles which, apparently, reflects a common trend in the chemistry of chalcogen-containing heterocyclic compounds. Whereas the methods of preparation and the reactions of benzo-1,3-diselenoles are mostly similar to those characteristic of benzo-1,3-dithioles, special features in the reactivity of telluroorganic compounds very often prevent their extension to the area of tellurium-containing heterocycles. Thus, the most general method of preparation of 2-substituted benzo-1,3-dithioles based on the acid-catalyzed condensation of benzene-1,2-dithiols with carbonyl compounds cannot be applied to the synthesis of benzo-1,3-ditelluroles considering the elusivenes of even the simplest tellurols which are thermally unstable species and extremely susceptible to oxidation. Moreover, some of the sulfur- and selenium-containing synthons important in the syntheses of derivatives of benzo-1,3-dithioles and benzo-1,3-diselenoles simply lack tellurium-containing analogs. Among these are carbon ditelluride, dialkyl ditellurocarbamates, benzotelluradiazoles, ethene-1,1-ditellurols, and others. On the other hand, the higher nucleophilicity of the benzene-1,2-selenolate and, in particular, of benzene-1,2-tellurolate dianions makes the substitution by these of halogens in geminal dihalohydrocarbons extremely facile.

2. A certain disproportion exists in the development of methods of synthesis of various derivatives of benzo-1,3-dichalcogenoles which were mostly intended to be a part of convenient procedures for the preparation of the precursors of dibenzotetrachalcogenafulvalenes. These include compounds such as benzo-1,3-dithiol- and diselenol-2-ones (-thiones, -selones), 2-(alkoxy)(alkylthio)-benzo-1,3-dithioles and benzo-1,3-dithiolylium salts. At the same time, rather scarce information has so far accumulated concerning the synthesis and reactions of other 2-substituted benzo-1,3-dichalcogenoles: (i.e. 2-NO_2-, CN-, COR-, and Hal-BDCs).

3. There is a need for a more systematic study and deeper insight into the mechanism and the synthetic application of the hydrolysis and the reduction of diverse 2-functionalized benzo-1,3-dithioles which possess a significant potential in the preparation of various carbonyl-containing compounds and difficultly accessible hydrocarbons. Of special interest would be a study of the chemical behavior of the corresponding derivatives of benzo-1,3-diselenole and -ditellurole.

4. In view of the finding that the "tetrachloroethylene" method of preparation of tetratellurafulvalenes and, most probably, also dibenzotetratellurafulvalenes leads to the formation of virtually inseparable mixtures of these compounds with their six-membered heterocyclic isomers, special attention must be paid to the development of alternative procedures based on precursors containing integrated 1,3-dichalcogenole moieties. Such a development is directly related to further progress in the chemistry of benzo-1,3-dichalcogenoles.

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