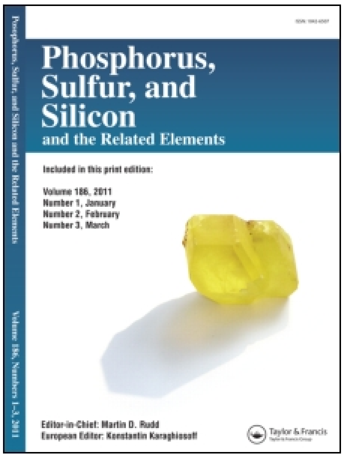

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Thiafulvenes and Thiafulvalenes in Organic Chemistry: Synthesis and Chemical Reactions

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To cite this Article Zayed, Salem E. , Hassan, M. Ezel-Dean and Ragab, Rawia(2007) 'Thiafulvenes and Thiafulvalenes in Organic Chemistry: Synthesis and Chemical Reactions', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 9, 1945 — 2007

To link to this Article: DOI: 10.1080/10426500701369831

URL: http://dx.doi.org/10.1080/10426500701369831

Phosphorus, Sulfur, and Silicon, 182:1945–2007, 2007
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701369831

Thiafulvenes and Thiafulvalenes in Organic Chemistry: Synthesis and Chemical Reactions

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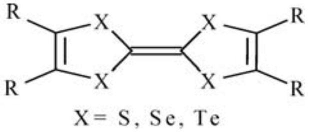
Fulvalenes and their derivatives have wide industrial, biological and therapeutic conductivity applications. The synthesis and chemistry of fulvalenes and derivatives starting with dithiolethiones, and main constituent of the fulvalenes moiety. I-Dithiol thiones: 1) 1,2-dithiolthiones: synthesis from 1,3-dithioles and from sulfur and nitrogen alkyl compounds by sulfuryl chloride. Reactions: photo-cycloadditions reactions, reactions with alkynes, and akylation reactions. 2) 1,3-dithiolthiones: ring synthesis from non heterocyclic compounds and heterocyclic compounds. Reactions: photochemical reactions, electrophilic attack at S-Nucleophilic attack at C. II-Fulvalenes: 1) Dithiafulvalenes; 2) Trithiafulvalenes; 3) Tetrathiafulvalenes.

Keywords Sulfur heterocycles; tetrathiafulvalenes; thiafulvalenes; trithiafulvenes

INTRODUCTION

Fulvalenes (**1**) and their derivatives are very interesting organic compounds due to their wide conductivity applications.[1–5]

(1)



Tetraheterofulvalenes containing oxygen, e.g. (**2**) increase the superconducting critical temperatures (Tc) of the fulvalene class of charge-transfer complexes.[6]

Received January 2, 2006; accepted March 16, 2007.

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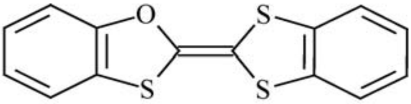
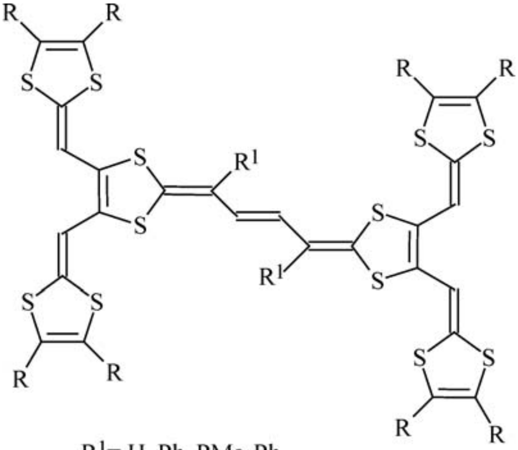
(2)



Cyclic voltammetry shows that compounds (**3**) are very strong π-donors and good precursors of conducting cation-radical salts.[7]



R^1= H, Ph, PMe-Ph
R or R-R= CO_2Me, $(CH{=}CH)_2$, H

(3)

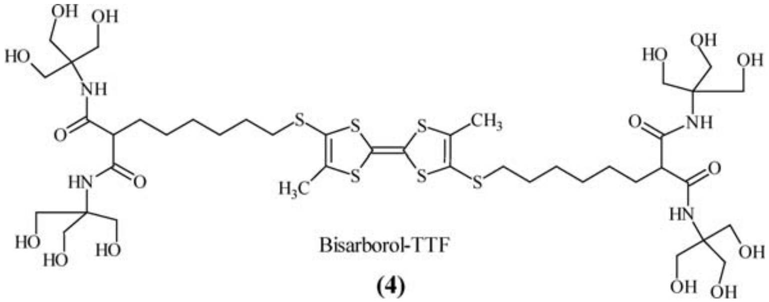
Tetrathiafulvalenes are electron donors that easily form charge-transfer complexes with electron acceptors such as radical salts, some of which possess a segregated structure (organic metals).[8]

The discovery of the exceptional electron conductivity of tetrathiafulvalenes TTF(s) has encouraged research into their synthesis. In addition to the original methods for the synthesis of TTF, there also exists the preparation of analogous compounds where all the hydrogens are substituted by alkyl, aryl, cycloalkyl, or alkylsulfanyl groups as well as those possessing electron-withdrawing groups.[8]

Recent developments in the field of creating conducting Langmuir-Blodgett films based on surface active charge transfer complexes and ion radical salts of organic electron donors and acceptors have stimulated interest in the synthesis of long-chain substituted derivatives of TTF.[9,10]

One of the interesting fields in organic materials is the preparation of molecular scale electronic and optical components such as rectifiers, switches, and wires.[11–13] These ultra small scale components have potential use in future generation computers and sensors.

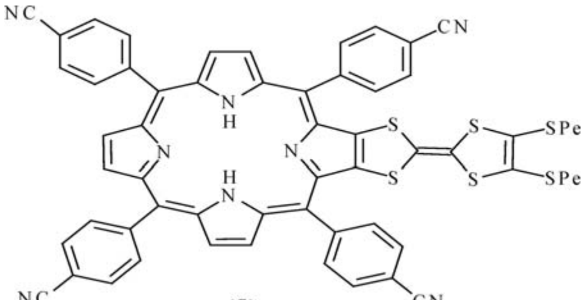
Molecular wires are in this context defined as molecular size conduits of electrons/holes with string-like structure. Bis arborol-TTF (**4**) is one of the several candidates for molecular wires.[14]



Bisarborol-TTF

(4)

Porphyrins[15] (e.g. mono-TTF-porphyrin (**5**))[16] play a central role in biological systems and find their expanding applications in materials science,[17] reaction catalysis,[18] molecular recognition,[19] and as diagnostic/therapeutic agents[20] and sensors.[21]



(5)

In addition there exist research areas dealing with the natural and synthetic 1,2-dithiole thiones with antioxidant, chemotherapeutic, radioprotective and cancer chemoprotective properties.[22] One substituted dithiolethione, Oltipraz [5-(2-(pyrazinyl)-4-methyl-1,2-dithiole-3-thione], originally an antischistosomal agent,[23] has been shown to protect against chemically induced carcinogenesis,[24] and was effective at inhibiting human immunodeficiency virus type-1 (HIV-1) replication.[25]

However, during the past few years, TTF and its derivatives have been incorporated into supramolecular systems such as chemical sensors,[26] charge separating ligands,[27] shuttles, and switches.[28]

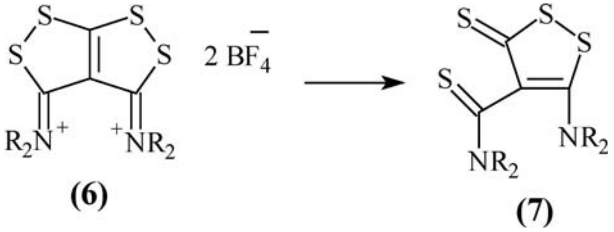
The following brief review of the synthesis and chemistry of fulvalenes and their derivatives, will be presented, starting with the synthesis and chemistry of 1,2- and 1,3-dithiolethiones, the main constituents of the fulvalene moiety.

(I) DITHIOLE COMPOUNDS

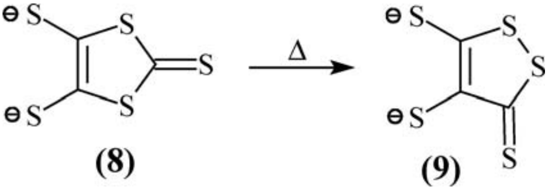
(1) 1,2-Dithiole-3-thiones

(A) Synthesis of 1,2-Dithiole-3-thiones

The thioamide derivatives (**7**) were obtained via heating (**6**) with aqueous hydrogen sulfide or with sodium salt of malononitrile.[29]

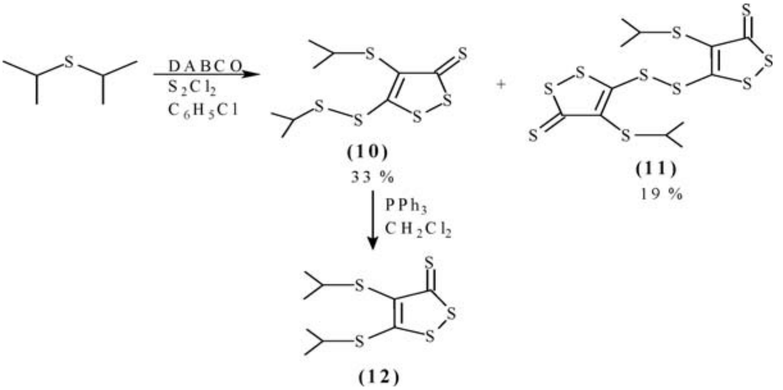


Meanwhile, the free alkali metal salts (**8**) are thermally unstable and undergo rearrangement to the corresponding salts of 1,2-dithiole-3-thione-4,5-dithiolates (**9**).[30]



Reaction of diisopropylsulfide and sulfuryl chloride (S_2Cl_2) in chlorobenzene in the presence of 1,4-diazabicyclo[2.2.2.]octane (DABCO) gives 4-isopropylthio-5-isopropyldithio-1,2-dithiole-3-thione (**10**) and the dimeric 5,5′-dithiobis(4-isopropylthio-1,2-dithiole-3-thione) (**11**). Treatment of (**10**) with triphenylphosphine gave compound (**12**).[31]

Also, reaction of N-(2-chloroethyl)diisopropylamine (**13**) and S_2Cl_2 in THF for 3 days at room temperature followed by sulfurization with P_4S_{10} and heating, gave 1,2-dithiole complex (**14**). Furthermore, compound (**13**) gave the thione (**17**) through the intermediates (**15**)–(**16**)[32] (Scheme 1).

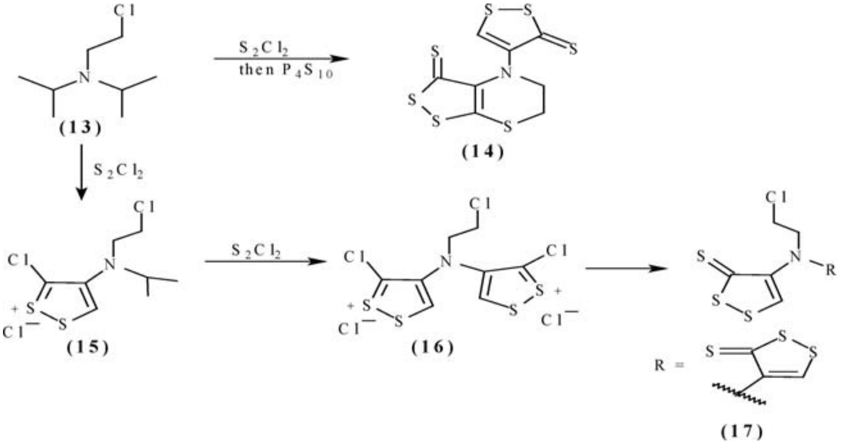


(B) Reactions of 1,2-Dithiole-3-thiones

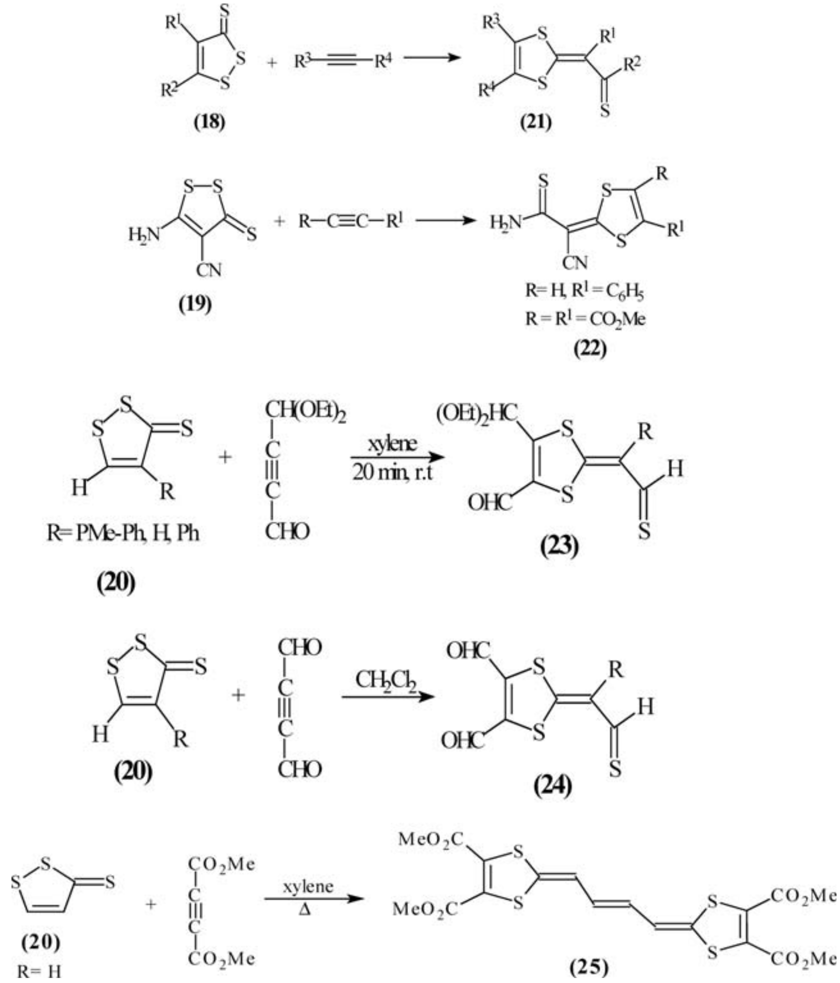
1,2-Dithiole-3-thione derivatives (**18–20**) are good substrates for the synthesis of 1,3-dithioles (**21–25**) when reacted with alkynes (Scheme 2).[7,33,34–36]

Photocycloaddition reactions have been used for the transformation of 1,2-dithiole-3-thiones (**26**) in the presence of alkenes to the corresponding 1,3-dithiolanes (**27**).[8]

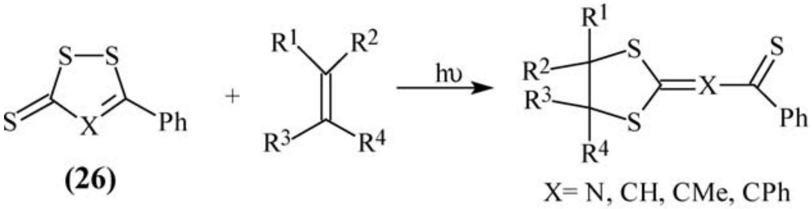
Alkylation of 4-mercapto-5-methylthio-1,2-dithiole-3-thione (**28**) (2 equiv.) with 1,8-dibromo-3,6-dioxaoctane (**29**) and 1,11-dibromo-3,6,9-trioxaundecane (**30**), respectively , in the presence of Cs_2CO_3 in DMF,[37] gives (**31**, **32**).

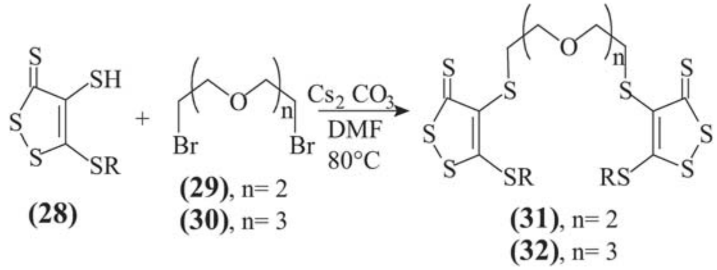


SCHEME 1


(18)
(21)
(19)
R= H, $R^1 = C_6H_5$
$R = R^1 = CO_2Me$
(22)
R= PMe-Ph, H, Ph
(20)
xylene
20 min, r.t
(23)
(20)
CH_2Cl_2
(24)
(20)
R= H
xylene
Δ
(25)

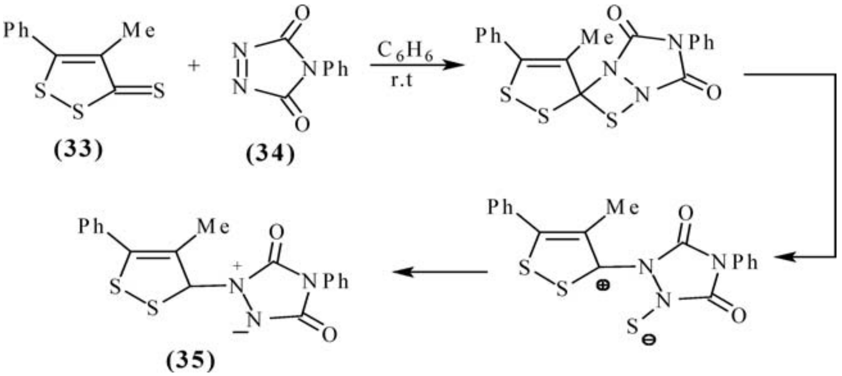
SCHEME 2


(26)
hυ
X= N, CH, CMe, CPh
(27)



(28) **(29)**, n= 2 **(30)**, n= 3 **(31)**, n= 2 **(32)**, n= 3

The reaction of 1,2-dithiole-3-thione (**33**) with N-phenyl triazinedione (**34**) afforded (**35**)[38] (Scheme 3).

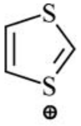


(33) **(34)** **(35)**

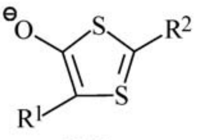
SCHEME 3

(2) 1,3-Dithioles

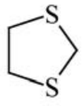
1,3-Dithiole species (**36–39**) are compounds that have gained a central position in the chemistry of new solid conducting materials.



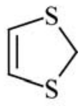
(36)



(37)



(38)

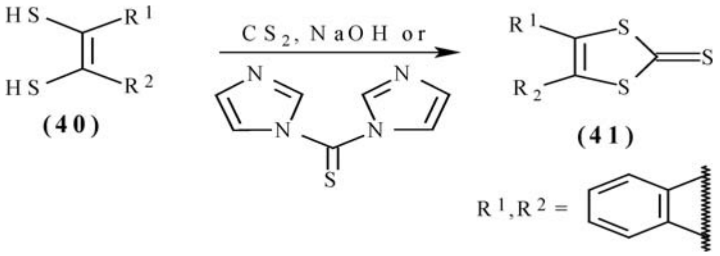


(39)

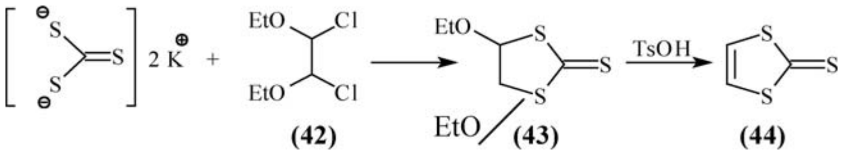
(A) Ring Synthesis

(a) From Nonheterocyclic Compounds. Benzo-anellated 1,3-dithiole-2-thiones (**41**) were obtained by the reaction of the dithioles

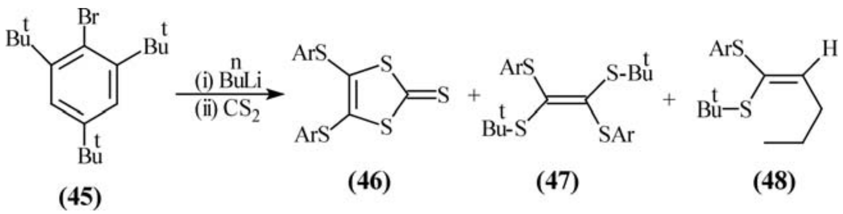
(**40**) with thiocarbonyldiimidazole in glacial acetic acid or with carbon disulfide in alkaline solution.[39]



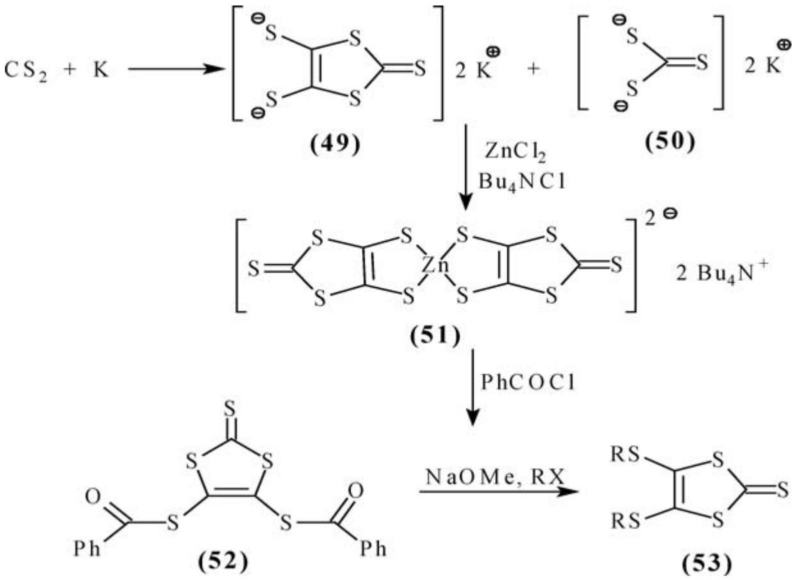
The precursor 1,3-dithiole-2-thione (**44**) can be accessed from the reaction of 1,2-dichloro-1,2-diethoxy-ethane (**42**) and potassium trithiocarbonate via formation of the intermediate[40] (**43**).



1-Bromo-2,4,6-tri-t-butylbenzene (**45**) gave on treatment with n-butyllithium a halogen metal exchange reaction to afford 2,4,6-tri-t-butyl phenyllithium which reacts with carbondisulfide at −78°C to give (**46**), (**47**) and (**48**).[41]

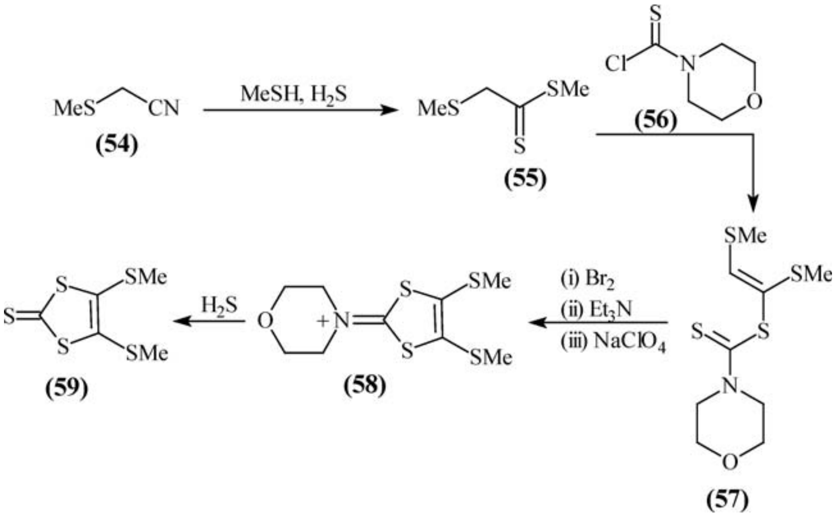


Reduction of carbon disulfide with potassium metal in DMF gives 4,5-dithio-1,3-dithiole-2-thione dianion (**49**) together with significant amounts of potassium trithiocarbonate (**50**). Treatment of the dianion (**49**) with tetra-n-butylammonium chloride/zinc chloride gave the tetra-n-butylammonium-zinchelate (**51**). Benzoylation of (**51**) affords the 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (**52**). Upon deacylation of (**52**) with sodium methoxide followed by alkylation, yields the corresponding 4,5-bis(alkyl-sulfanyl)-1,3-dithiole-2-thiones (**53**)[40] (Scheme 4).



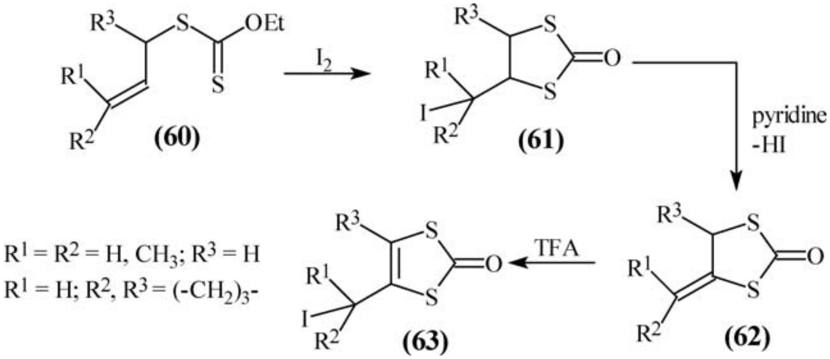
SCHEME 4

The heterocyclic compound (**56**) was also utilized for synthesis of 4,5-bis(methyl-sulfanyl)-1,3-dithiole-2-thione (**59**) from 2-methylsulfanylacetonitrile (**54**) via its reaction with alkyl thione (**55**) followed by a sequence steps[41] (Scheme 5).



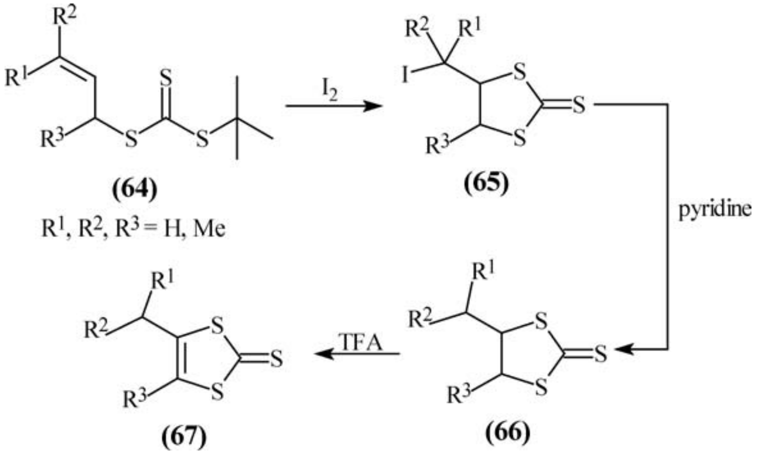
SCHEME 5

The unsaturated dithiocarbonates (**60**) upon reaction with iodine gave dithiolanone derivatives (**61**) while elimination of hydrogen iodide gives (**62**). Treatment of (**62**) with trifluoroacetic acid resulted in the formation of 1,3-dithiole-2-ones (**63**)[42] (Scheme 6).

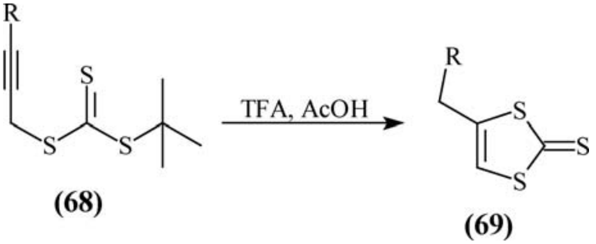


SCHEME 6

Allyl-t-butyltrithiocarbonates (**64**) could also be cyclised with loss of hydrogen iodide and isobutylene using elemental iodine to 1,3-dithiolane-2-thiones (**65**). Treatment of (**65**) with pyridine resulted in loss of hydrogen iodide and (**66**) was obtained. Isomerization of (**66**) using trifluoroacetic acid also afforded (**67**).[43]

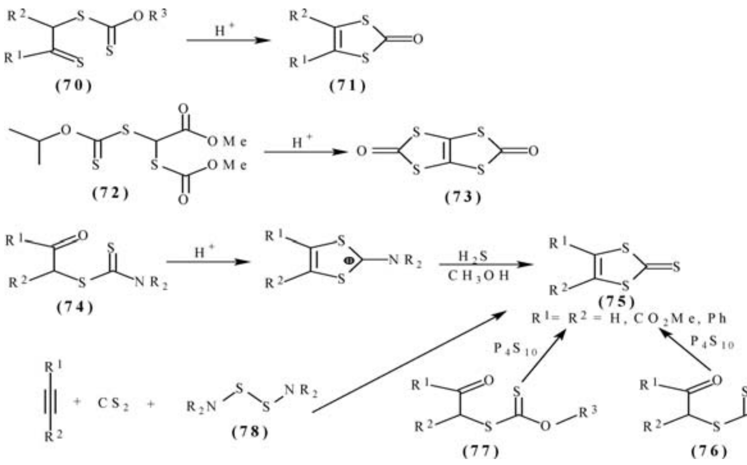


Ring-closure of propargyl-t-butyltrithiocarbonates (**68**) in presence of a mixture of trifluoroacetic acid/glacial acetic acid gave (**69**).[43]



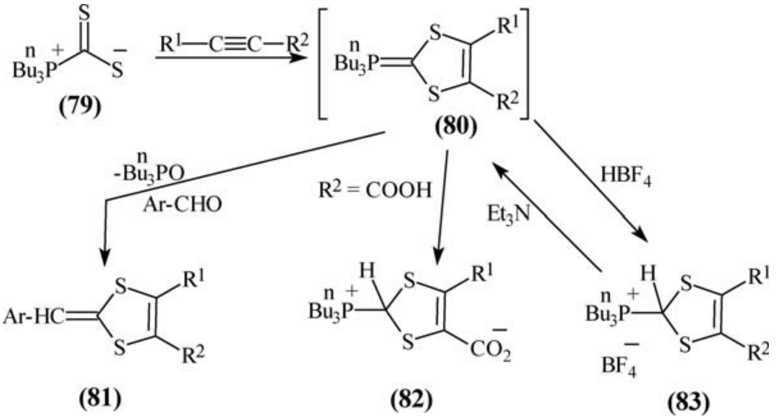
Acid catalyzed cyclization of (**70**), (**72**) and (**74**) using concentrated sulfuric acid led to the formation of (**71**), (**73**), and (**75**), respectively. The latter could also be obtained from the reaction of (**76**) or (**77**) with tetraphosphorus decasulfide in boiling decaline.[40,42–44]

Also, sequence reaction of carbon disulfide with alkynes in the presence of bis(amino)disulfides (**78**) at 140°C in a steel autoclave afforded 1,3-dithiole-2-thiones (**75**)[40] (Scheme 7).



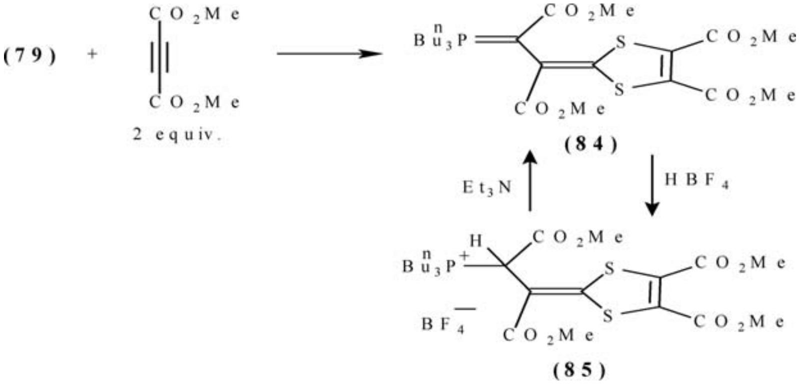
SCHEME 7

Formation of 2-alkylidene-1,3-dithioles (**81**) was reported upon reaction of (**79**) with dimethylacetylenedicarboxylate (DMAD) in the presence of aromatic aldehydes via formation of the intermediate (**80**). Addition of (**80**) to acetylenedicarboxylic acid was accompanied by intramolecular proton transfer in the initial adducts (**80**) to give (**82**). Intermolecular protonation of (**80**) was also possible by carrying out the addition of DMAD in the presence of HBF_4. The resulting stable salt (**83**) acts as a convenient source of (**80**) by simple treatment with Et_3N and this has allowed the use of (**80**) in the construction of a variety of tetrathiafulvalene analogues of interest as electron donors for organic conductors[45–47] (Scheme 8).

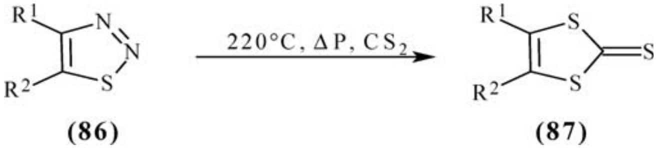


SCHEME 8

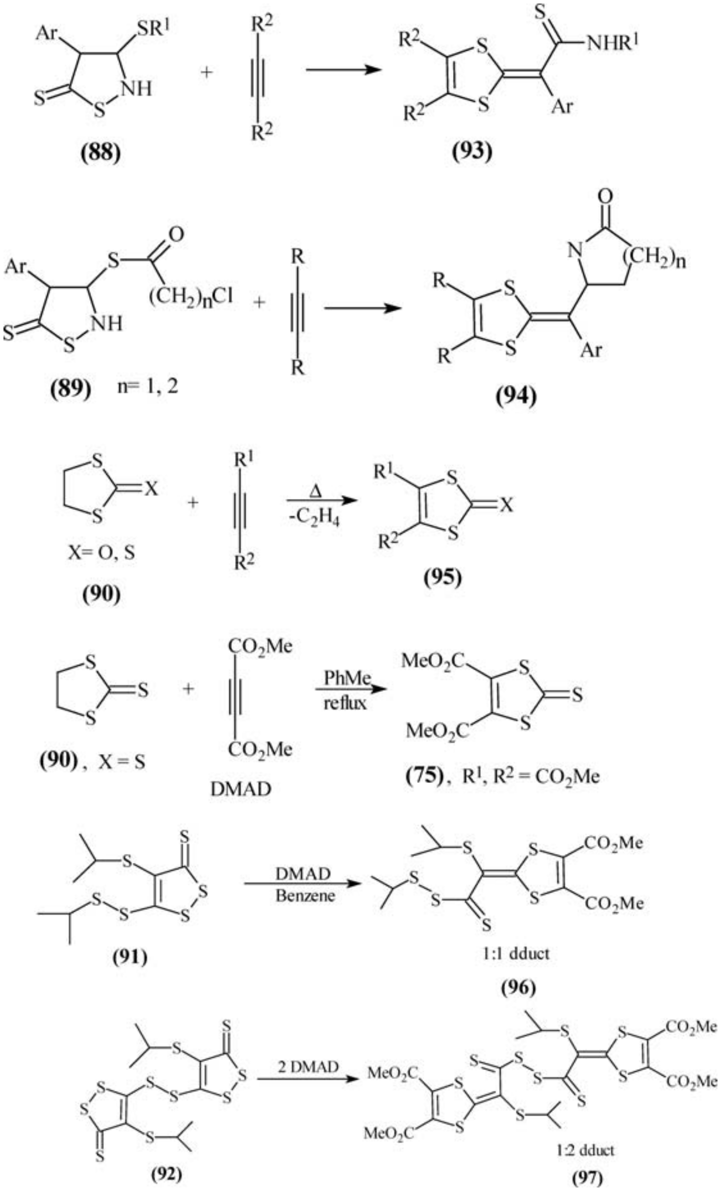
Formation of 1:2 adduct (**84**) was reported via the reaction of (**79**) with 2 equivalents of DMAD. The adduct (**84**) was readily converted to the conjugate phosphonium salt (**85**) on treatment with mineral acids and can be formed from them with a weak base , e.g., Et_3N^{48}.



(b) From Heterocyclic Compounds. Thermolysis of 1,2,3-thiadiazoles (**86**) in carbon disulfide under forced conditions provides a synthetic route to trimethylene-, tetramethylene-and benzo-1,3-dithiole-2-thiones (**87**).[49]

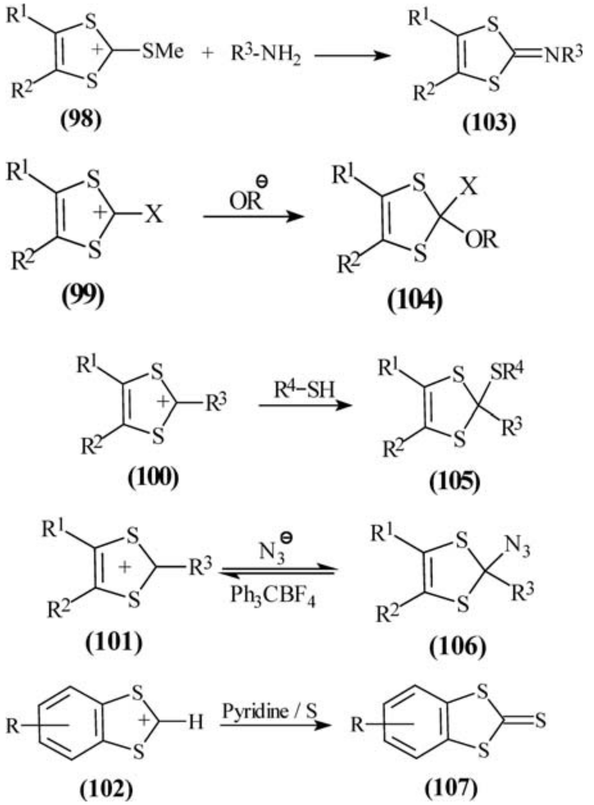


Reactive alkylnic compounds furnished formation of 1,3-dithioles (**93–97**) through their reaction with a variety of reagents (**88–92**)[31,33,50] (Scheme 9).



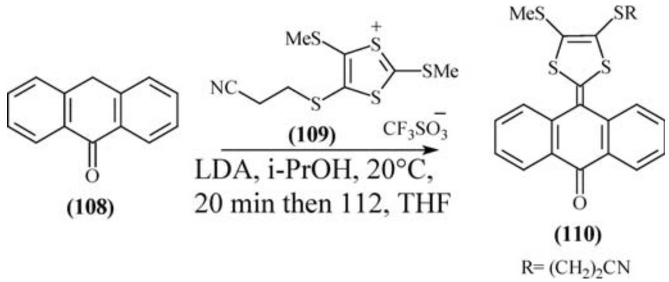
SCHEME 9

Also, 1,3-dithiolium salts (**98–102**) reacted with primary amines, alcohols or alcoholates, thioles, azides and elemental sulfur to give the corresponding 1,3-dithioles (**103–107**)[51–54] (Scheme 10).

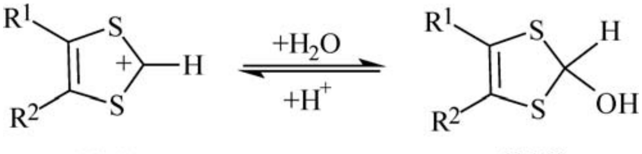


SCHEME 10

1,3-Dithiolium cation salt (**109**) was prepared by methylation of the corresponding thione. Reaction of (**109**) with the anion of the anthrone (**108**) afforded compound (**110**).[55]

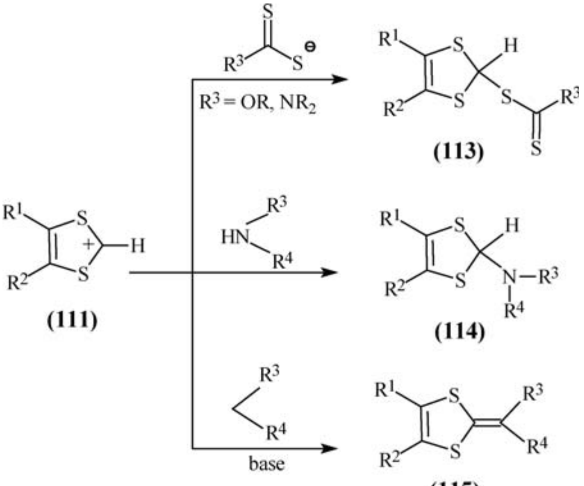


A reversible reaction was detected on hydrolysis of 1,3-dithiolium cations (**111**) to give the corresponding 2-hydroxy-1,3-dithioles (**112**). Treatment of (**112**) with acid afforded again the adducts (**111**).[52]



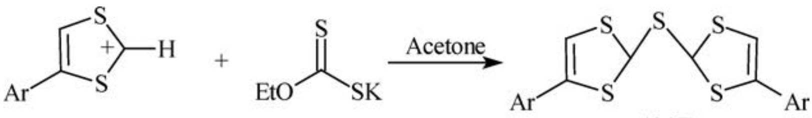
(111) **(112)**

Furthermore, O-alkyldithiocarbonate and dithiocarbamate anions, secondary amines and activated methylene groups when reacted with (**111**) gave the corresponding 1,3-dithioles[51,53,56] (**113–115**) (Scheme 11).



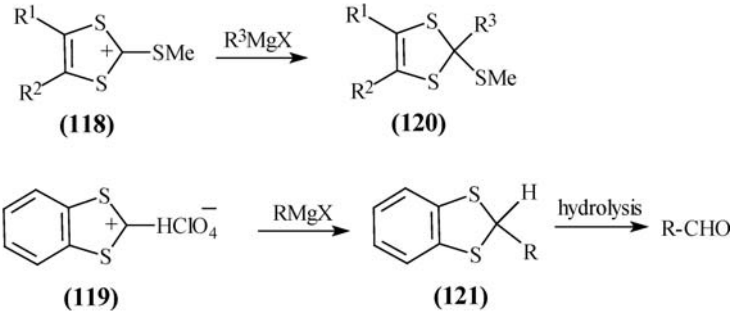
SCHEME 11

Meanwhile, 4-aryl-1,3-dithiolium salts (**116**) afforded (**117**) upon reaction with excess potassium-o-ethyl dithiocarbamate in acetone.[53]



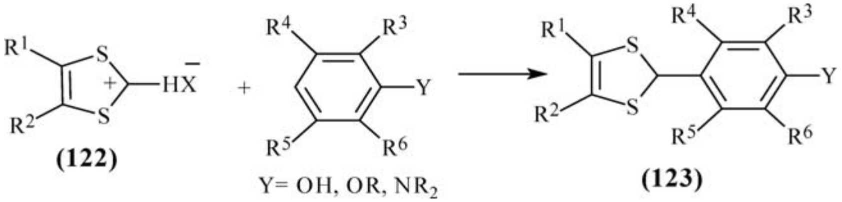
(116) **(117)**

Grignard reagents when allowed to react with 1,3-dithiolium salts (**118–119**), formed the corresponding 1,3-dithioles[55,57] (**120–121**) (Scheme 12).

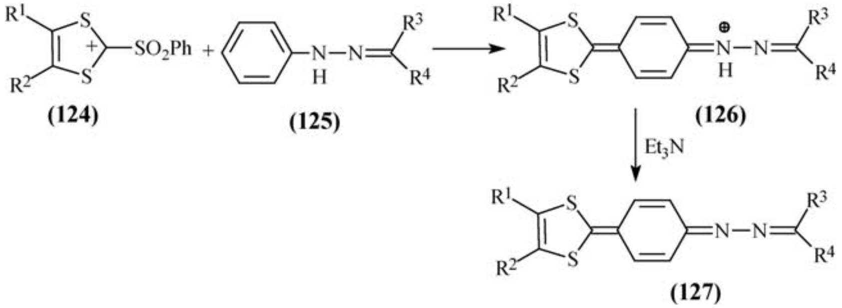


SCHEME 12

Arylamines, phenols, and phenolethers were also reacted with their electron-rich para-position at C-2 of 1,3-dithiolium ion (**122**) and gave compounds of the type (**123**).[57]

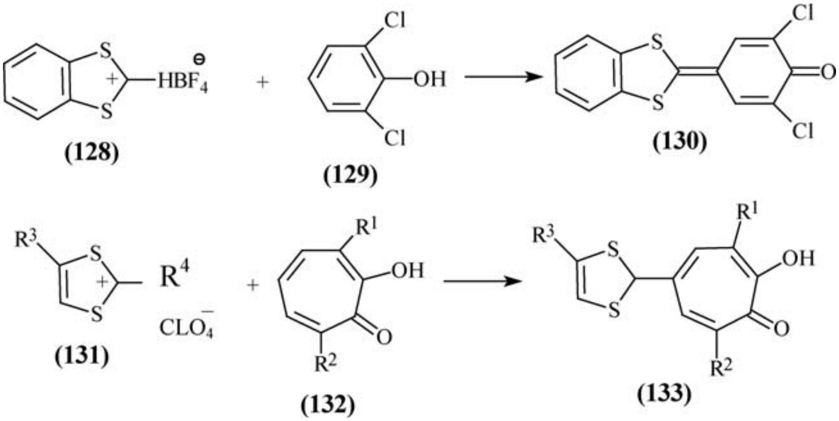


Compound (**126**) was easily prepared via the reaction of arylhydrazones (**125**) with 2-methylsulfonyl-or 2-phenylsulphonyl-1,3-dithiolium salts (**124**). Deprotonation of (**126**) with Et_3N afforded (**127**).[29]



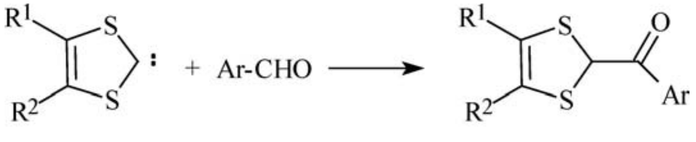
The quinonoid system (**130**) was obtained on treatment of 1,3-benzodithiolium tetrafluoroborate (**128**) with an excess of 2,6-

dichlorophenol (**129**), while 2-(4-hydroxy-5-oxo-1,3,5-cycloheptatrienyl)-4-phenyl-1,3-dithioles (**133**) were obtained upon reaction of 4-phenyl-1,3-dithiolium perchlorate (**131**) with tropolones (**132**)[57] (Scheme 13).



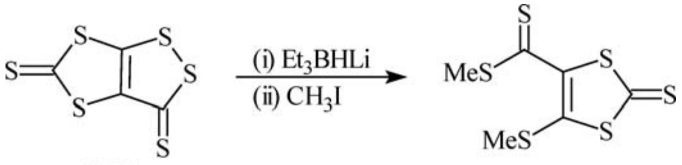
SCHEME 13

The carbenes (**134**) could also be trapped with aromatic aldehydes to yield 2-aroyl-1,3-dithioles (**135**).[51]



(134) (135)

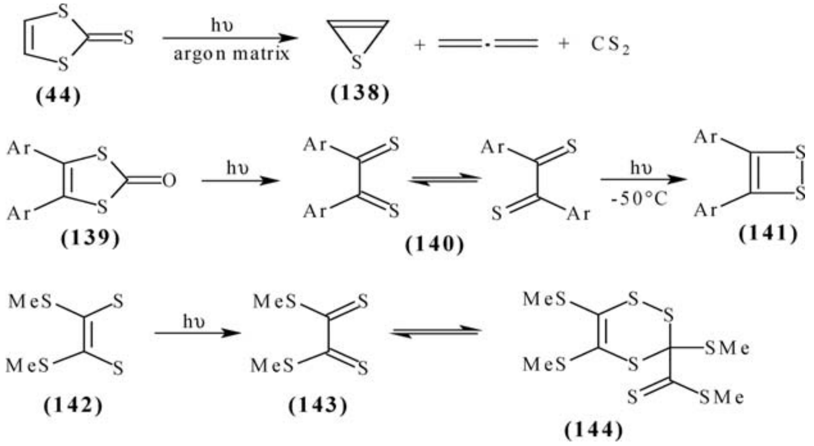
Reaction of heterocycle (**136**) with Et_3BHLi followed by treatment with methyl iodide afforded the monocyclic sulfur-containing compound (**137**) via ring opening.[58]



(136) (137)

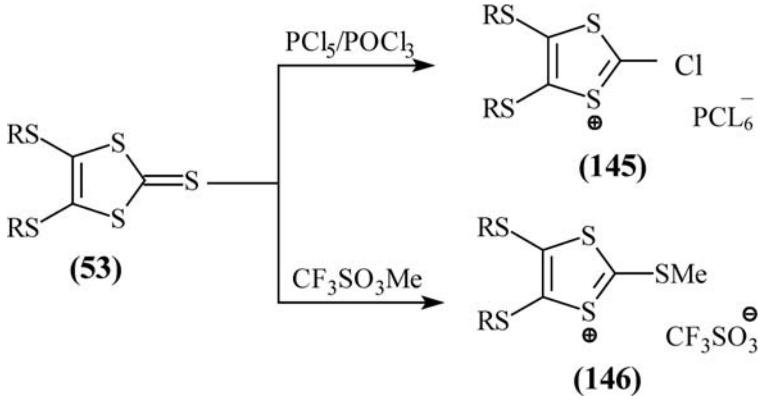
(B) REACTIONS OF 1,3-DITHIOLES

Photochemical Reactions. Irradiation of the 1,3-dithiole-2-thione (**44**) afforded the antiaromatic thiirene (**138**) in an argon matrix, while photolysis of the 1,3-dithiole-2-one (**139**) afforded the dithione derivative (**140**) in two isomeric forms. Further irradiation at −50°C yields a product believed to be a dithiete (**141**). Similarly, the dithiolone (**142**) gave the tetrathiooxalate (**143**) which is in equilibrium with its [4+2] dimer (**144**) (Scheme 14).[59,60]

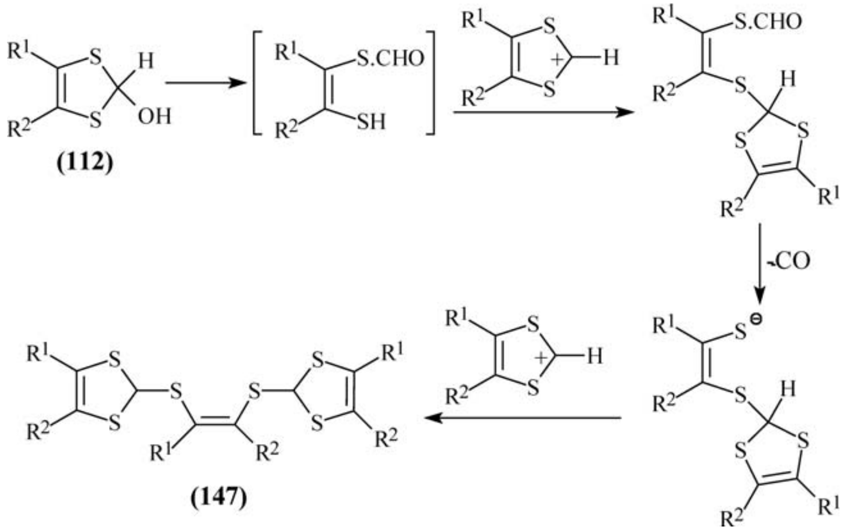


SCHEME 14

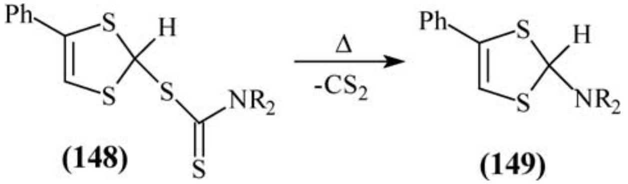
Electrophilic Attack at Sulfur. 4,5-Bis(alkylsulfanyl)-1,3-dithiole-2-thiones (**53**) were transformed into (**146**) by using methyltriflate and gave upon reaction with phosphorus pentachloride in phosphorus oxychloride, the corresponding 2-chloro-4,5-bis(alkylsulfanyl)-1,3-dithiolium hexa-chlorophosphate (**145**).[59]



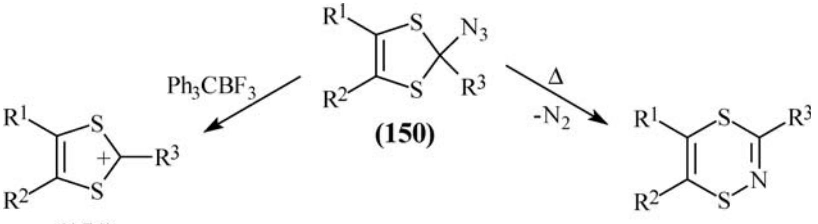
Nucleophilic Attack at Carbon---With O-Nucleophiles. The 2-hydroxy-1,3-dithioles (**112**) are quite unstable compounds leading by reaction with excess of 1,3-dithiolium ions to a variety of products (**147**).[53]



With S-Nucleophiles. The 2-(amino-thiocarbonylthio)-4-phenyl-1,3-dithioles (**148**) upon heating afford carbon disulfide and the N-substituted-2-amino-4-phenyl-1,3-dithioles (**149**).[54]

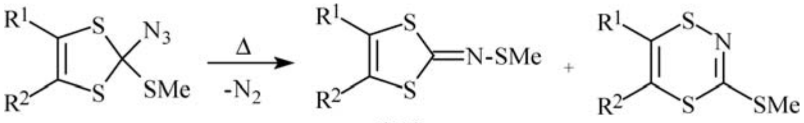


With N-Nucleophiles. 2-Azido-1,3-dithioles (**150**) upon reaction with triphenylmethyl tetrafluoroborate afforded azido-triphenylmethane and the corresponding 1,3-dithiolium salt (**151**), whereas upon thermal treatment of (**150**), nitrogen liberates and 1,4,2-dithiazines (**152**) were obtained.[55]



(151) **(150)** **(152)**

In analogy, thermal treatment of 2-azido-2-methylsulfanyl-1,3-dithioles (**153**) afforded a mixture of 2-imino-1,3-dithiole (**154**) and 1,4,2-dithiazines (**155**).[55]

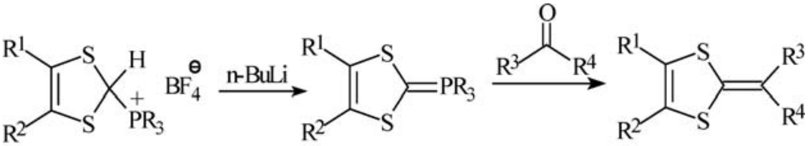


(153) **(154)** **(155)**

With C-Nucleophiles. 2-Alkyl-2-S-methyl-1,3-dithioles (**156**) when reacted with excess Grignard reagents gave 2,2-dialkyl-1,3-dithioles (**157**).[55]

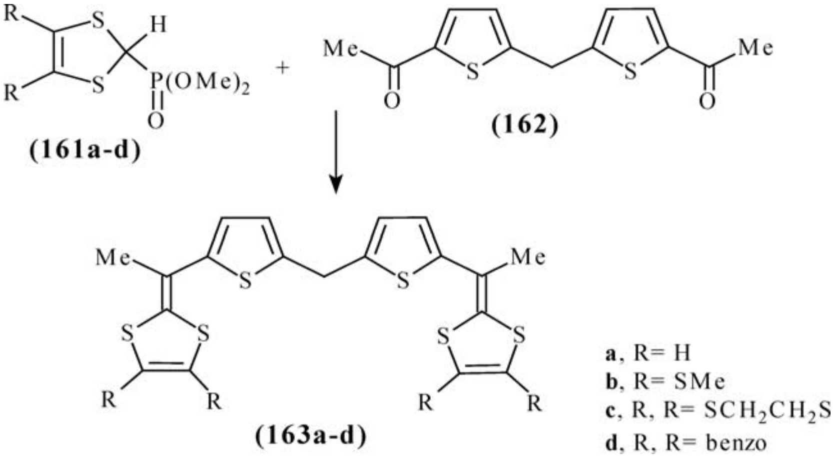
(156) **(157)**

With P-Nucleophiles. 2-Phosphoiono-1,3-dithiolium salts (**158**) are valuable starting materials in reactions leading via (**159**) to compound (**160**).[61]



(158) **(159)** **(160)**

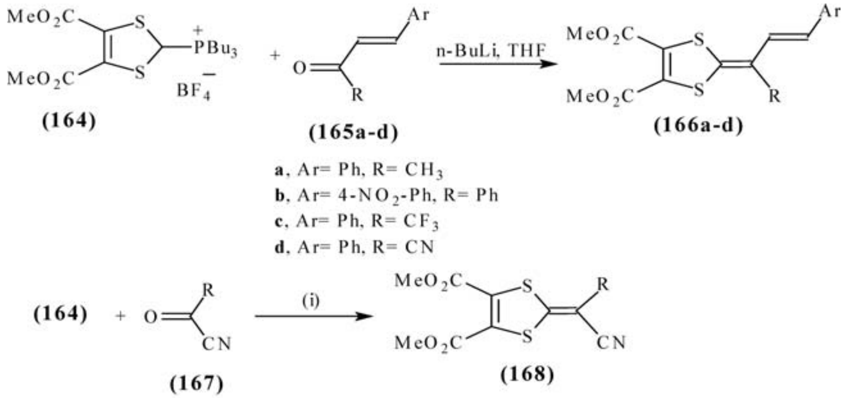
The new compounds (**163a–d**) were prepared by Wittig-Horner reaction of the corresponding carbanions derived from phosphonate esters (**161a–d**) with ketone (**162**).[62]



a, R= H
b, R= SMe
c, R, R= SCH_2CH_2S
d, R, R= benzo

Addition of compound (**165a–c**) to a mixture of 1,3-dithiole Wittig reagent (**164**) in presence of n-butyllithium led to the formation of π-extended compounds (**166a–c**).

Under the same reaction condition, reaction of the reagent (**164**) with (**167**) gave the alkenes (**168**).[63]

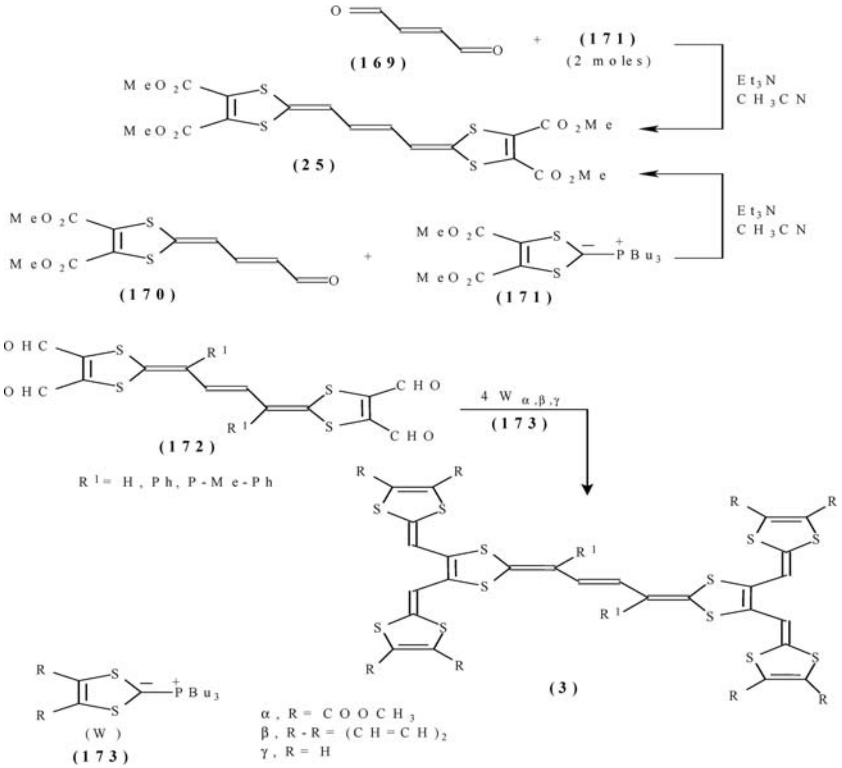


a, Ar= Ph, R= CH_3
b, Ar= 4-NO_2-Ph, R= Ph
c, Ar= Ph, R= CF_3
d, Ar= Ph, R= CN

R= CH_3, Ph, 4-Cl-Ph, 4-MeO-Ph
(i) **164**, Et_3N or n-BuLi, THF, **167**

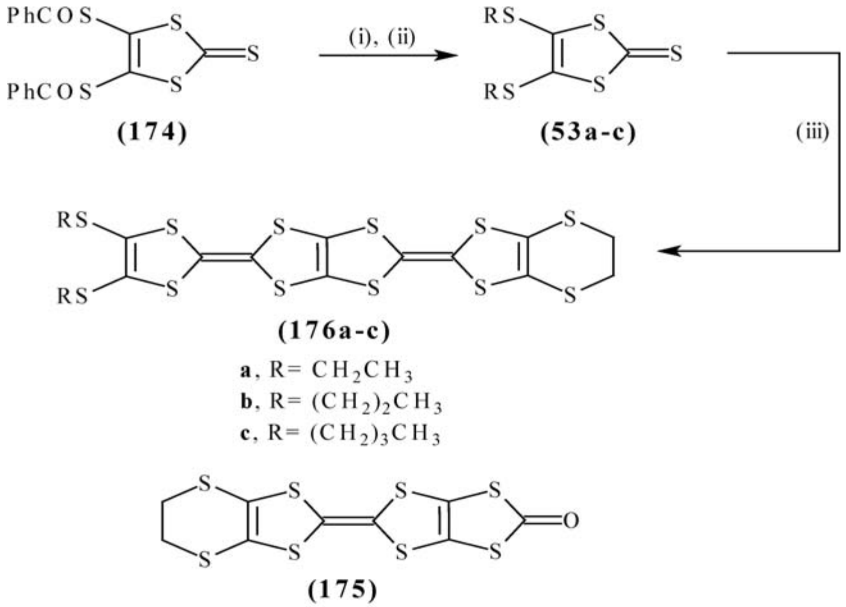
The tetraester (**25**) is produced from fumaric aldehyde (**169**) or the aldehyde (**170**) by bis- or mono-olifination with 1,3-dithiole Wittig reagent (**171**).[47]

Similarly, the fourfold Wittig olifination of (**172**) with P-ylids $W_{\alpha-\gamma}$ (**173**) afforded compound (**3**) which is a vinylogs of tetra-thiafulvalene[7] (Scheme 15).



SCHEME 15

4,5-Bis(alkylthio)-1,3-dithiole-2-thione derivatives (**53a–c**) were obtained through deprotection processes of 4,5-bis(benzothio)-1,3-dithiole-2-thione (**174**). The compounds (**53a-c**) and (**175**) were cross coupled in trimethylphosphite-toluene to give the corresponding (2-[4,5-bis-(alkylthio)-1,3-dithiole-2-ylidene]-5-(4,5-ethylenedithio-1,3-dithiole-2-ylidene)-1,3,4,6-tetrathiapentalene) TET-TTP (**176a–c**)[64] (Scheme 16).



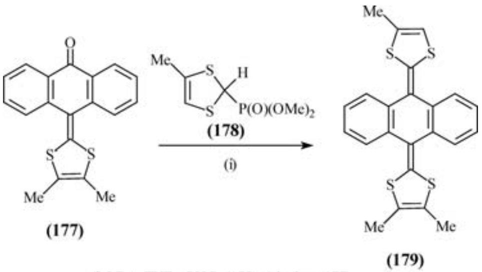
(174) **(53a-c)** **(176a-c)** **(175)**

a, R= CH_2CH_3
b, R= $(CH_2)_2CH_3$
c, R= $(CH_2)_3CH_3$

(i) MeONa, MeOH, r.t. 15 min
(ii) RBr, r.t, 1 h.
(iii) **(175)**, $P(OMe)_3$-toluene (1:1 v/v), 110°C, 2 h.

SCHEME 16

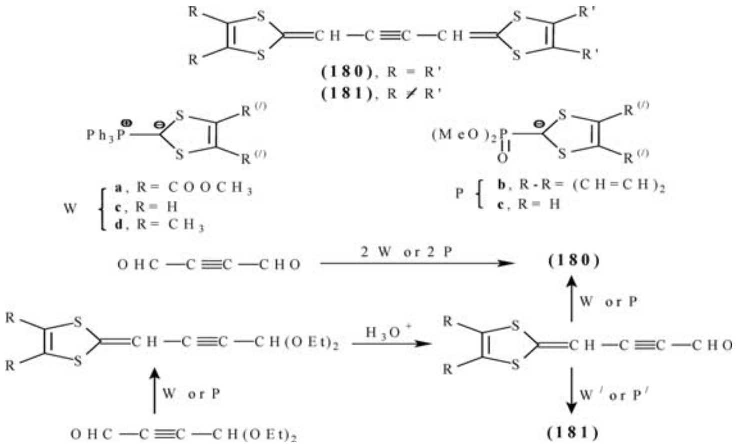
The trimethyl derivative of 9,10-bis(1,3-dithiole-2-ylidene)-9,10-dihydroanthracene system (**179**) was synthesised on reaction of (**177**) with the deprotonated phosphonate anion reagent (**178**).[55]



(177) **(178)** **(179)**

(i) LDA, THF, -78°C, **(178)**, 1 h. then **(177)**

Title compounds (Scheme 17) can be prepared through Wittig or Wittig-Horner reactions between phosphoranes (W) or phosphonate anions (P) bearing the 1,3-dithiole-2-ylidene moiety and acetylene-dicarbaldehyde or its acetal.[65]



SCHEME 17

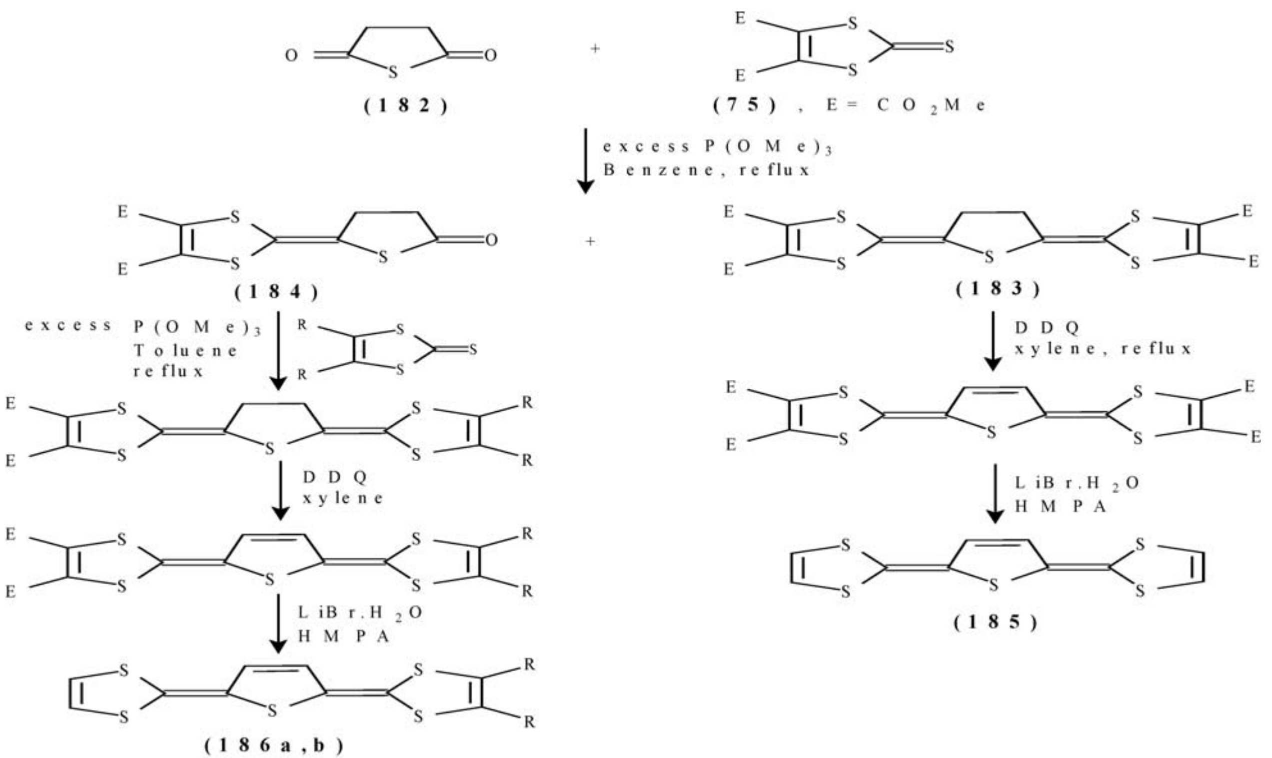
Reaction of the anhydride (**182**) with 4,5-bis(methoxycarbonyl-1,3-dithiole-2-thione (**75**) in the presence of excess trimethylphosphite in refluxing benzene afforded (**183**) and (**184**). A consequence reactions led to the formation of symmetrical and unsymmetrical derivatives (**185**) and (**186a**,**b**), respectively[66] (Scheme 18).

A series of (**189a-c**)[67] derivatives were obtained on treatment of (**182**) with the cyclic sulfur-containing compound (**187**) (Scheme 19).

Reaction of phosphorous reagent (**190**) with LDA in the presence of tetrahydrothiopyran-4-one (**191**) or 2,6-diphenyltetrahydrothiopyran-4-one (**192**) in THF at −78°C gave 1,3-dithiole-2-thione (**193**) or (**194**) which on reaction with an excess of mercury (II) acetate in chloroform-acetic acid afforded the corresponding 1,3-dithiole-2-ones (**195**) or (**196**). On coupling ketones (**195** and **196**) with various 1,3-dithiole-2-thiones (**197a–c**) in triethylphosphite at 80°C, the corresponding tetrahydro derivatives of (**195**) [**198a–c**] and (**196**) [**199a-c**] were obtained. Dehydrogenation of (**198**) and (**199**) gives (**200a–c**) and (**201a–c**)[68] (Scheme 20).

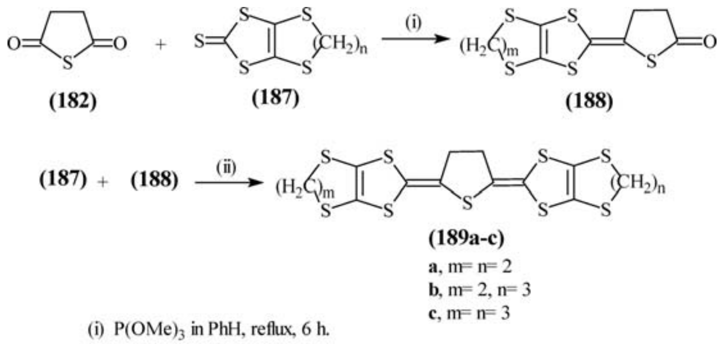
Anthraquinone (**202**) when allowed to react with the crown reagent (**203**) under standard conditions gave a mixture of bis-and mono-crown annelated derivatives (**204**) and (**205**). Reaction of (**203**) with (**206**) gave the bis(1,3-dithiole) system (**207**)[69] (Scheme 21).

The target donor molecules (**211–213**)**a–c** have been synthesized through Wittig or Wittig-Horner reactions between phosphorane or phosphonate anions bearing the 1,3-dithiole-2-ylidene moiety and compounds (**208**), (**209**) and (**210**)[70] (Scheme 22).



a, R-R = SCH$_2$CH$_2$S
b, R = SMe

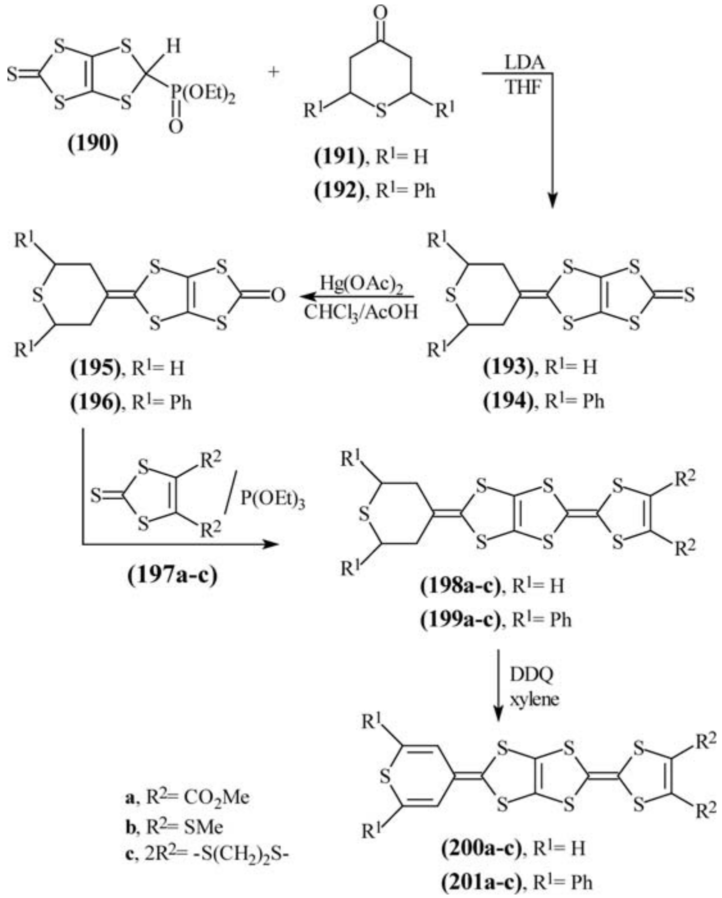
SCHEME 18



a, m= n= 2
b, m= 2, n= 3
c, m= n= 3

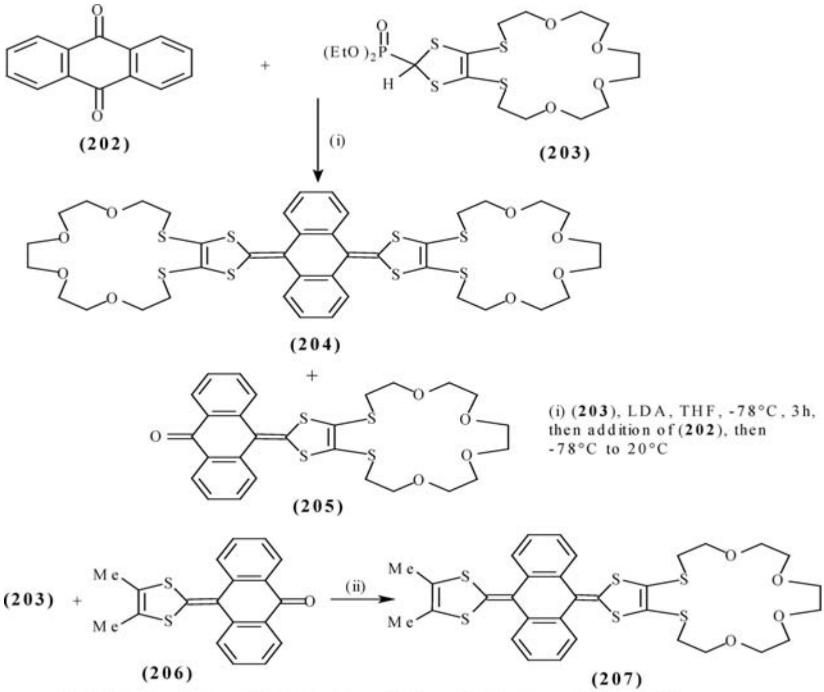
(i) $P(OMe)_3$ in PhH, reflux, 6 h.
(ii) $P(OMe)_3$ in PhH, reflux, 18 h.

SCHEME 19



a, R^2= CO_2Me
b, R^2= SMe
c, $2R^2$= $-S(CH_2)_2S-$

SCHEME 20



(i) (**203**), LDA, THF, -78°C, 3h, then addition of (**202**), then -78°C to 20°C

(ii) (**203**), LDA, THF, -78°C, 3h., then addition of (**206**), then -78°C to 20°C

SCHEME 21

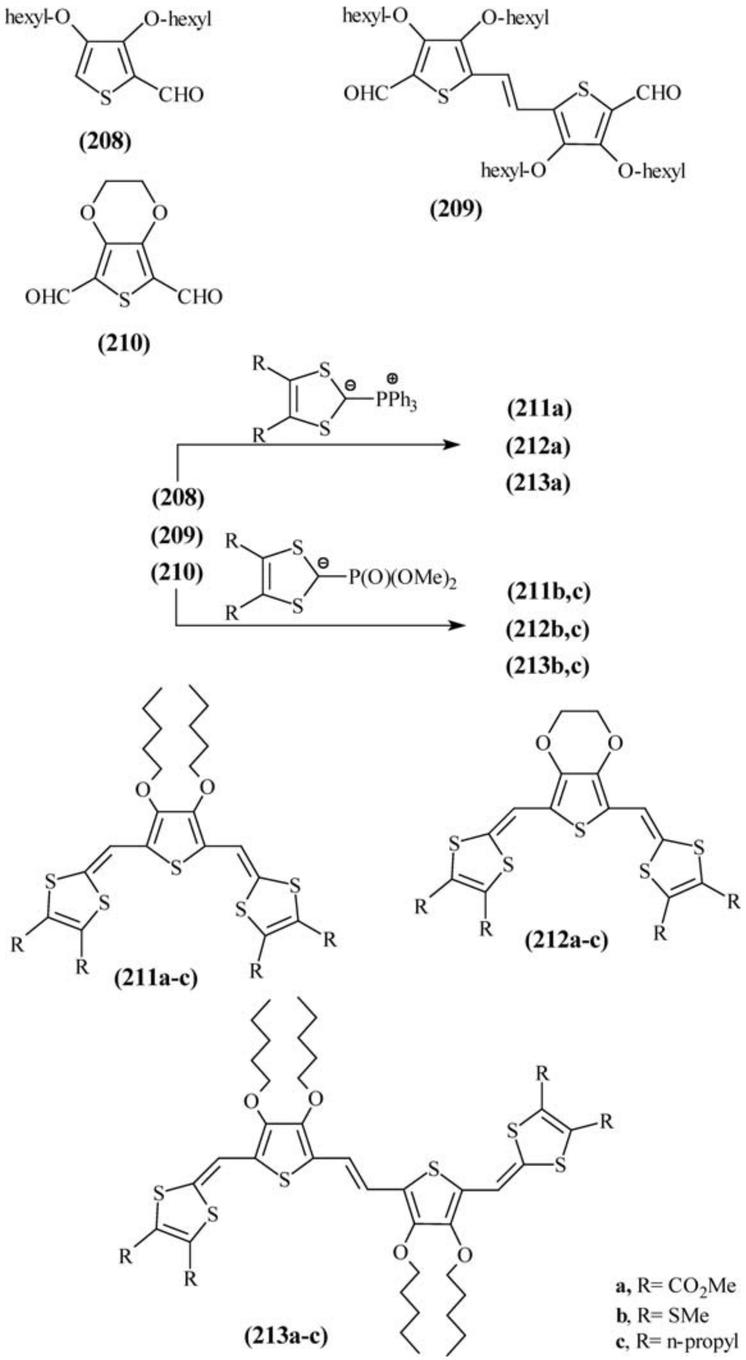
Nitroso compound (**215**) could be obtained in good yield upon reaction of phosphonium salt (**164**) with 2-(nitrosoformylmethylene)-4,5-dicarbomethoxy-1,3-dithiole (**214**). Oxidation of (**214**) took place preferentially at the nitroso function and was converted by m-chloroperbenzoic acid (m-CPBA) into the nitroaldehyde (**216**) which underwent a Wittig reaction with (**164**) to produce the desired(**217**). The reaction of (**215**) with isoamyl nitrite afforded the dinitroso structure (**218**). Formation of (**218**) by this method is always accompanied by production of the nitroso nitro compound (**219**)[71] (Scheme 23).

(II) FULVALENES

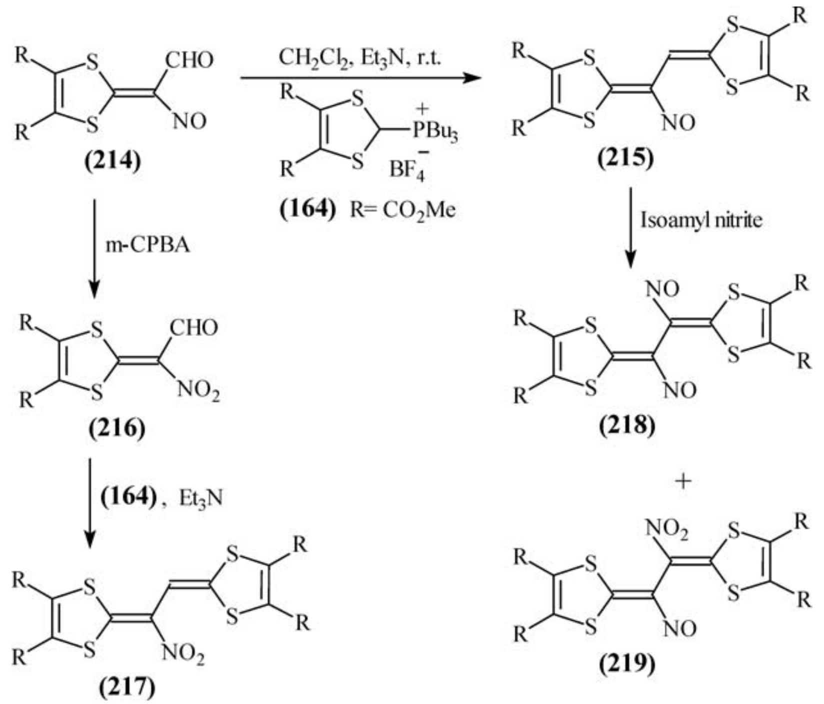
(1) Dithiafulvalenes

Synthesis of Dithiafulvalenes

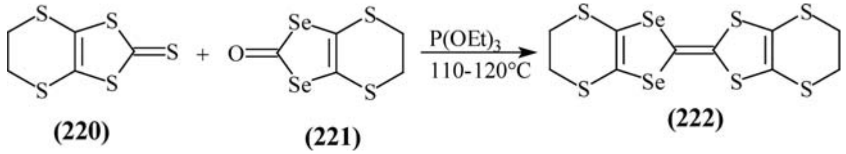
Unsymmetrical donor bis(ethylenedithio)diselenadithiafulvalene (**222**) has been synthesized through the reaction of 4,5-ethylenedithio-1,3-diselenol-2-one (**221**) and 4,5-ethylenedithio-1,3-dithiole-2-thione (**220**) in triethylphosphite.[72]


hexyl-O
O-hexyl
S
CHO
(208)
hexyl-O
O-hexyl
OHC
S
S
CHO
hexyl-O
O-hexyl
(209)
O
O
OHC
S
CHO
(210)
R
S
S
R
⊖
⊕
PPh$_3$
(211a)
(212a)
(213a)
(208)
(209)
(210)
R
S
S
R
⊖
P(O)(OMe)$_2$
(211b,c)
(212b,c)
(213b,c)
(211a-c)
(212a-c)
(213a-c)
a, R= CO$_2$Me
b, R= SMe
c, R= n-propyl

SCHEME 22



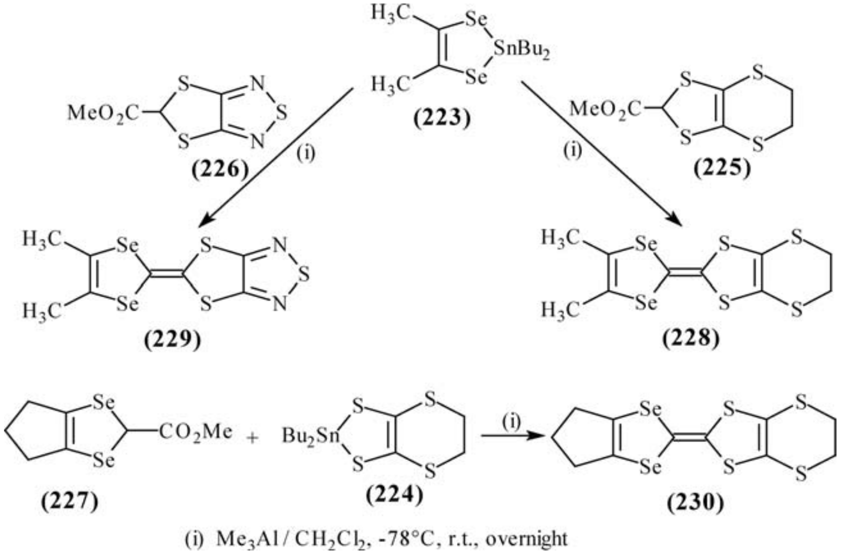
SCHEME 23



In addition, the synthesis of diselenadithiafulvalene derivatives (**228–230**) could be accomplished by Me_3Al-mediated reaction of selenolate (**223**) or tin thiolate (**224**) with esters (**225**), (**226**) and (**227**)[73] (Scheme 24).

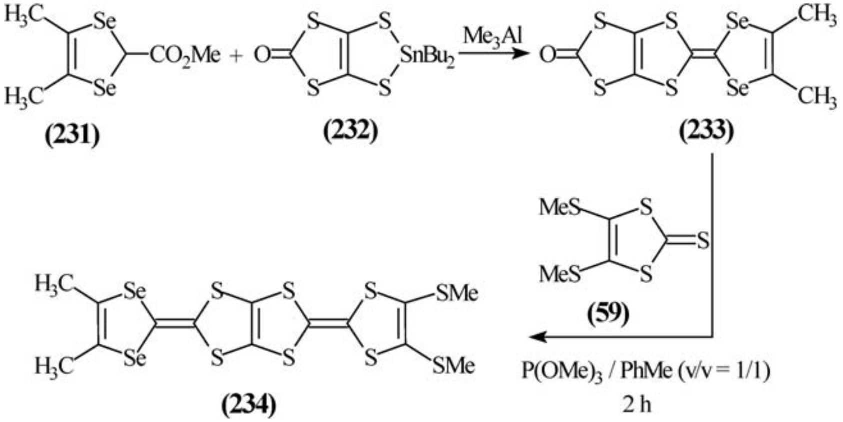
Furthermore, the application of the Me_3Al-promoted reaction of tin thiolate (**232**) with ester (**231**) for the synthesis of unsymmetrical TTF-fused donor enabled to obtain TTF-fused system (**234**) in short steps[73] (Scheme 25).

Also, a novel selenium-containing bis-fused TTF donor (**237**) has been synthesized as shown in Scheme (26).[74]

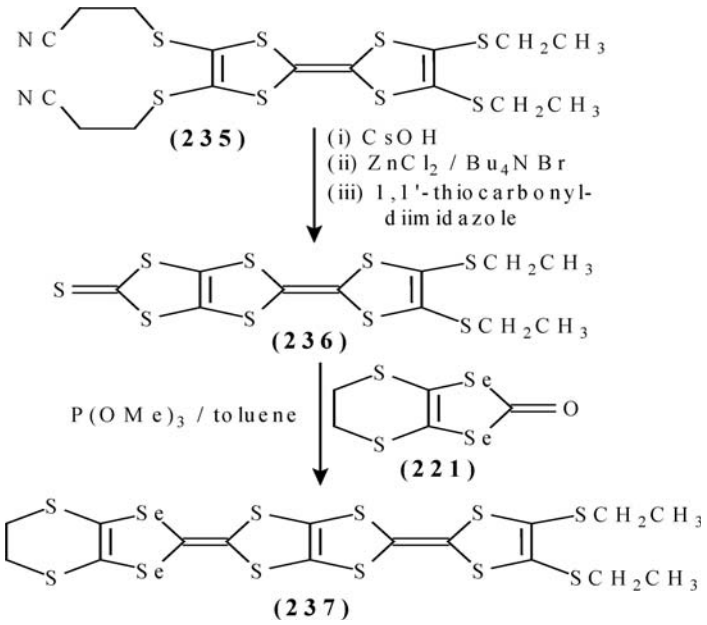


SCHEME 24

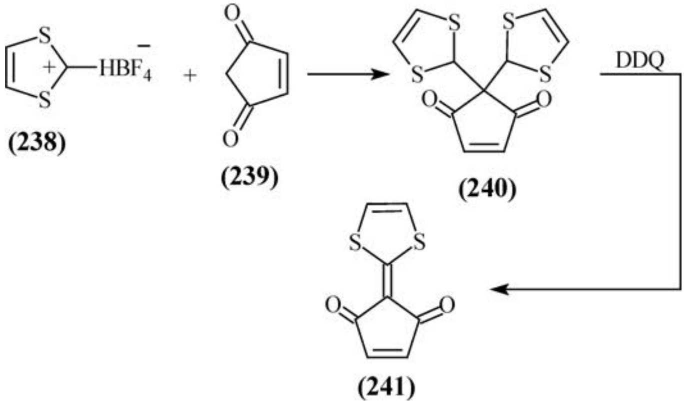
1,3-Dithiolium tetrafluoroborate (**238**) when reacted with 2-cyclopentene-1,4-dione (**239**), the product (**240**) was formed. Oxidation of (**240**) using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) yielded dithiafulvalene derivative (**241**).[56]



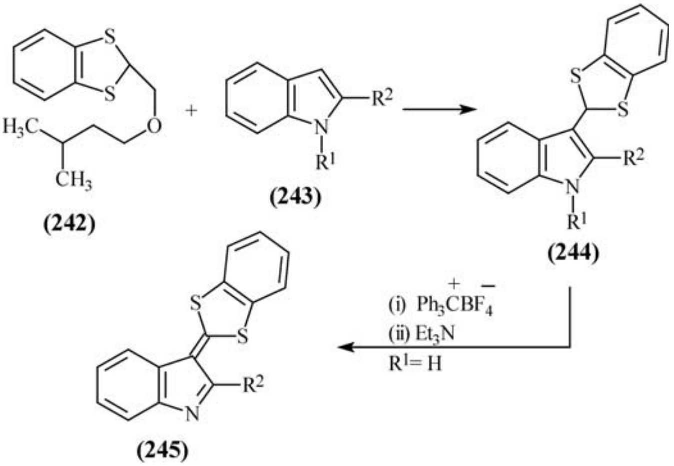
SCHEME 25



SCHEME 26



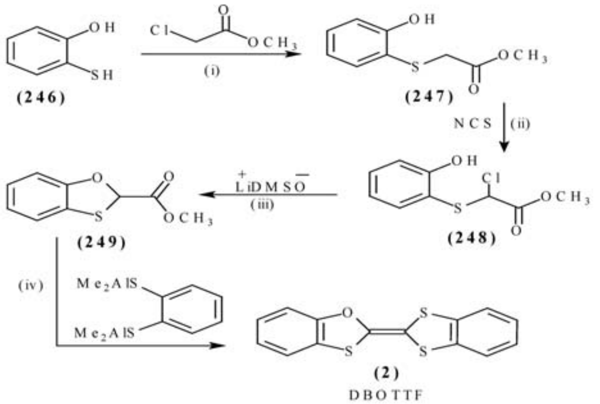
Also, reaction of benzodithiole (**242**) with indole derivative (**243**) in acetic acid gave the substitution products (**244**). Consecutive treatment of (**244**) with triphenylmethyltetrafluoroborate and Et_3N afforded the dibenzo-1,4-dithia-6-azafulvalene[75] (**245**).



(2) Trithiafulvalenes

Synthesis of Trithiafulvalenes

Tetraheterofulvalenes containing oxygen have been synthesized for increasing the superconducting critical temperatures (Tc) of the fulvalene class of charge-transfer (C-T) complexes. DBOTTF (**2**) was targeted as a simple model for a more general synthesis of oxatrithiafulvalene derivatives[6] (Scheme 27).



(i) toluene, 5 equiv. $ClCH_2COOCH_3$, 1.2 eq. NEt_3, r.t., 16 h., chrom. silica / CH_2Cl_2

(ii) 50% $CHCl_3$ / 50% CCl_4, 1 eq. NCS, r.t., 2h.

(iii) DMSO, 1 eq. n-BuLi, r.t, 30 min.

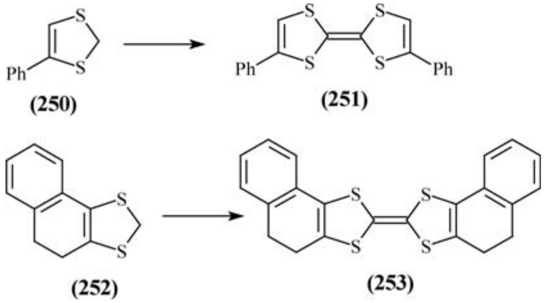
(iv) CH_2Cl_2, 0.5 eq. O-$[(H_3C)_2AlS]_2C_6H_4$, 40°C, 5 min., chrom. silica / CCl_4 in the dark.

SCHEME 27

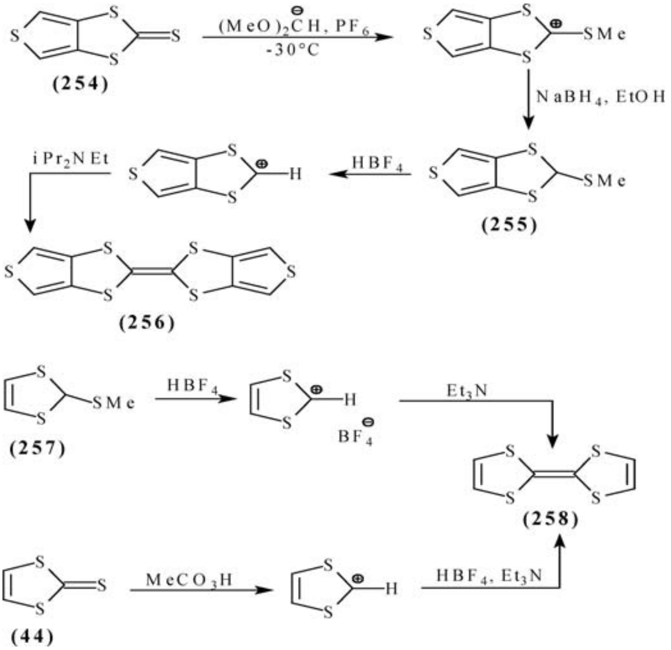
(3) Tetrathiafulvalenes

(A) Synthesis

The synthesis of TTF by pyridine-assisted electrochemical oxidation of dihydrotetrathiafulvalenes has only been described for 1,3-dithioles with an aryl substituent in the 4-position as examplified by the transformation of (**250**) and (**252**) to afford (**251**) and (**253**), respectively.[76]



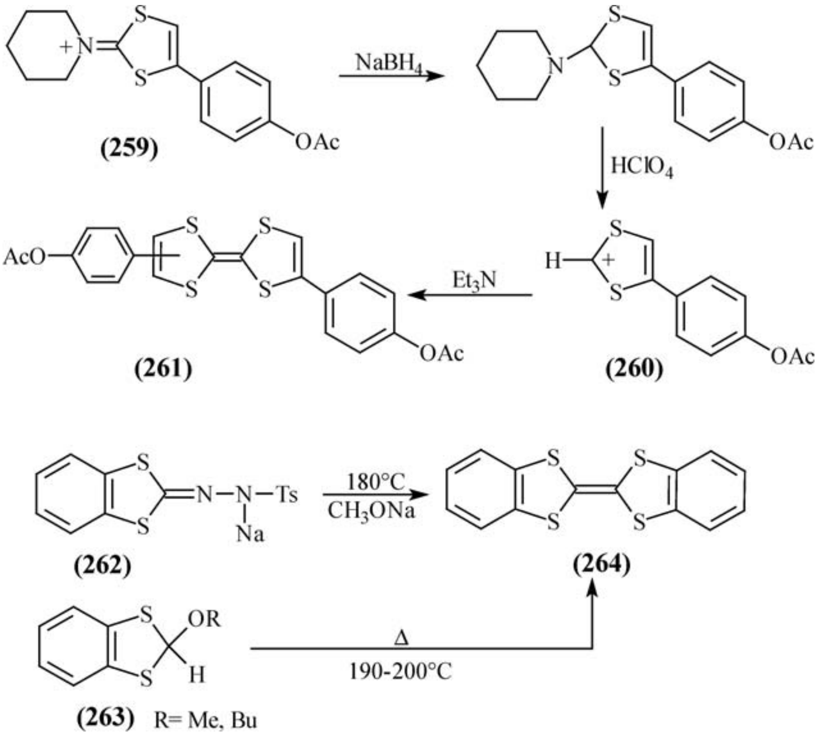
The synthesis of TTF (**256**) and (**258**) via elimination of a proton in 1,3-dithiolium salts in the final synthetic step involves the reaction of a carbene or of a phosphorous ylide on a 1,3-dithiolium salt possessing a hydrogen at C(2). These adducts can be accessed either by alkylation



SCHEME 28

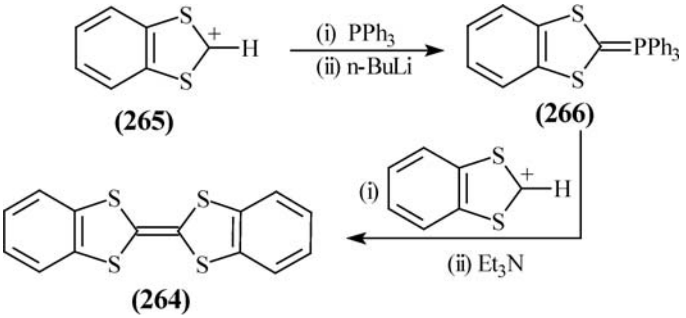
of suitable 2-thioxo-1,3-dithiolium salts or by oxidation of a 2-thioxo-1,3-dithiole (**44**) by peracid or by hydrogen peroxide in acetic acid[76] (Scheme 28).

1,3-Dithiolium salts (**260**) were obtained from 1,3-dithiolium salts (**259**) via reduction with sodium borohydride followed by reaction with strong acid. Deprotonation of (**260**) affords the corresponding TTF (**261**). Also, dibenzo-TTF (**264**) has been obtained by pyrolysis of either 2-imino-1,3-benzodithiole (**262**) in the presence of one equivalent of sodium methoxide in diglyme at 180°C or pyrolysis of suitable 2-alkoxy-1,3-benzothioles (**263**) at 190–200°C[77] (Scheme 29).

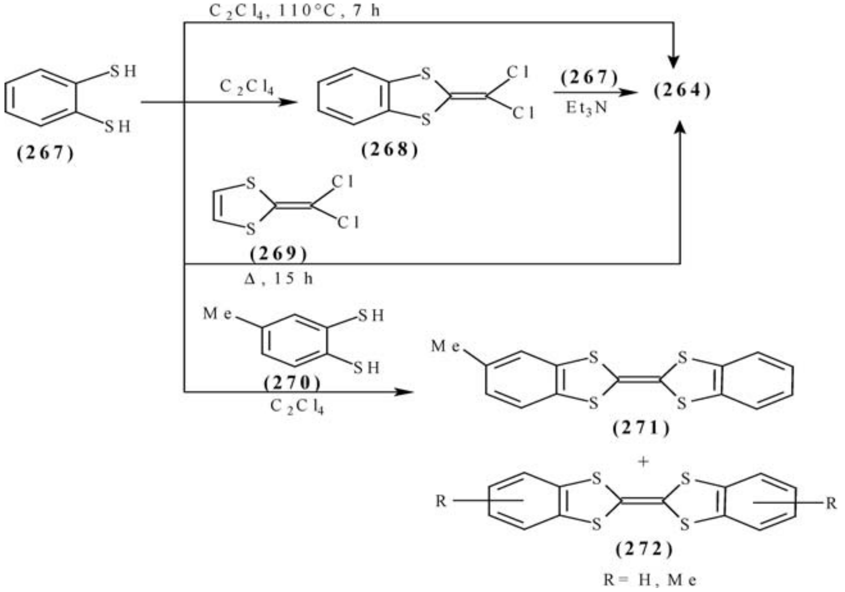


SCHEME 29

1,3-Dithiolium salts (**265**) react with 2-triphenylphospheno-1,3-dithiole (**266**) to afford unisolatable intermediates, which give dibenzo-TTF (**264**) upon treatment with base at low temperatures. This method also permits the selective preparation of unsymmetrical TTF.[78]

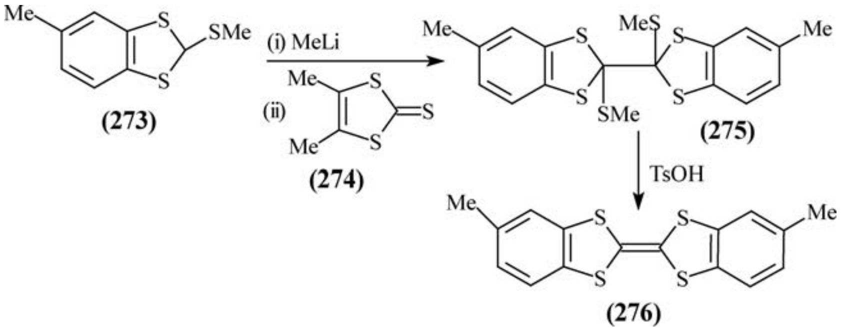


Dibenzo-TTF was also obtained through the reactions of tetrachloroethylene with 1,2-benzenedithioles[79] (**267**) (Scheme 30).

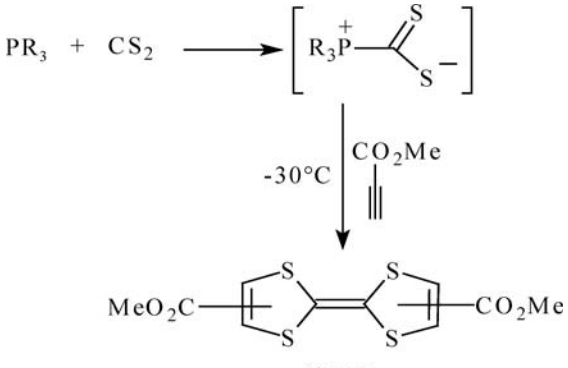


SCHEME 30

Moreover, TTF derivative (**276**) could be obtained via reaction of the lithiated product (**273**) with the trithione (**274**). The intermediate (**275**) upon treated with toluenesulphonic acid gave the dimer (**276**).[80]



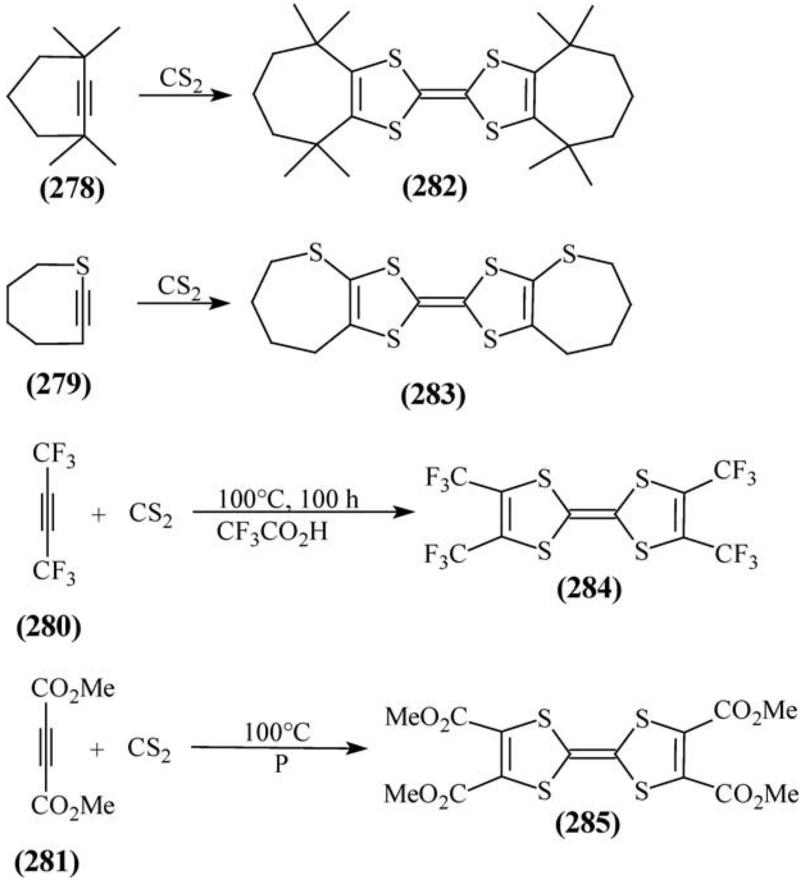
Similarly, TTF (**277**) was obtained from trialkylphosphanes and alkynes in the presence of carbon disulfide.[78]



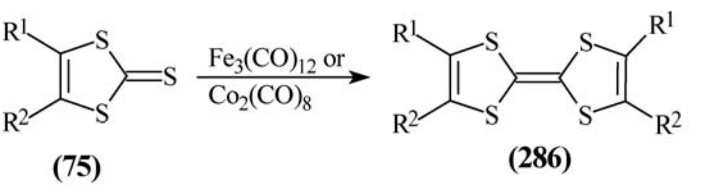
(277)

A new series of TTF (**282–285**) were synthesized through the action of carbon disulfide on the strained (**278–281**)[77] (Scheme 31).

Reaction of (un)substituted 2-thioxo-1,3-dithioles (**75**) with iron carbonyl $Fe_3(CO)_{12}$ or more efficiently with dicobalt octacarbonyl led to the synthesis of (un)substituted TTF[80] (**286**).

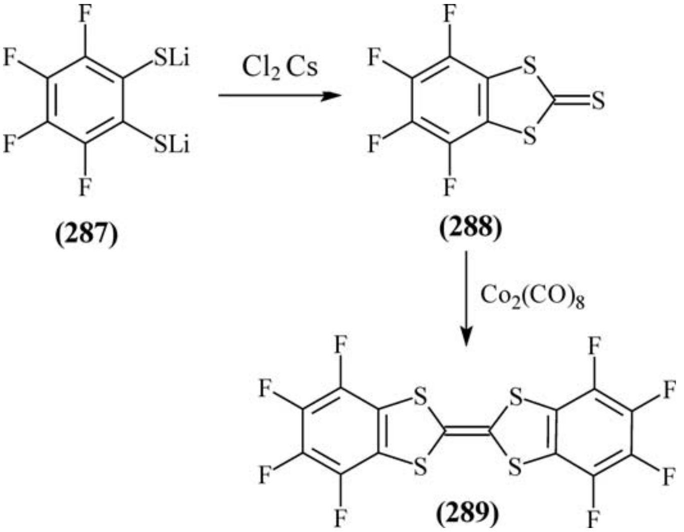


SCHEME 31



$R^1, R^2 = H, Me, Ph, CN, CO_2Me$

For the synthesis of octafluorodibenzo-TTF (**289**), $Co_2(CO)_8$ has been used in the key step to afford the desired TTF.[80]



Alternatively, 1,3-dithioles (**290–293**) react with trivalent phosphorus compounds to form the corresponding TTF derivatives[80,81] (**294–298**) (Scheme 32).

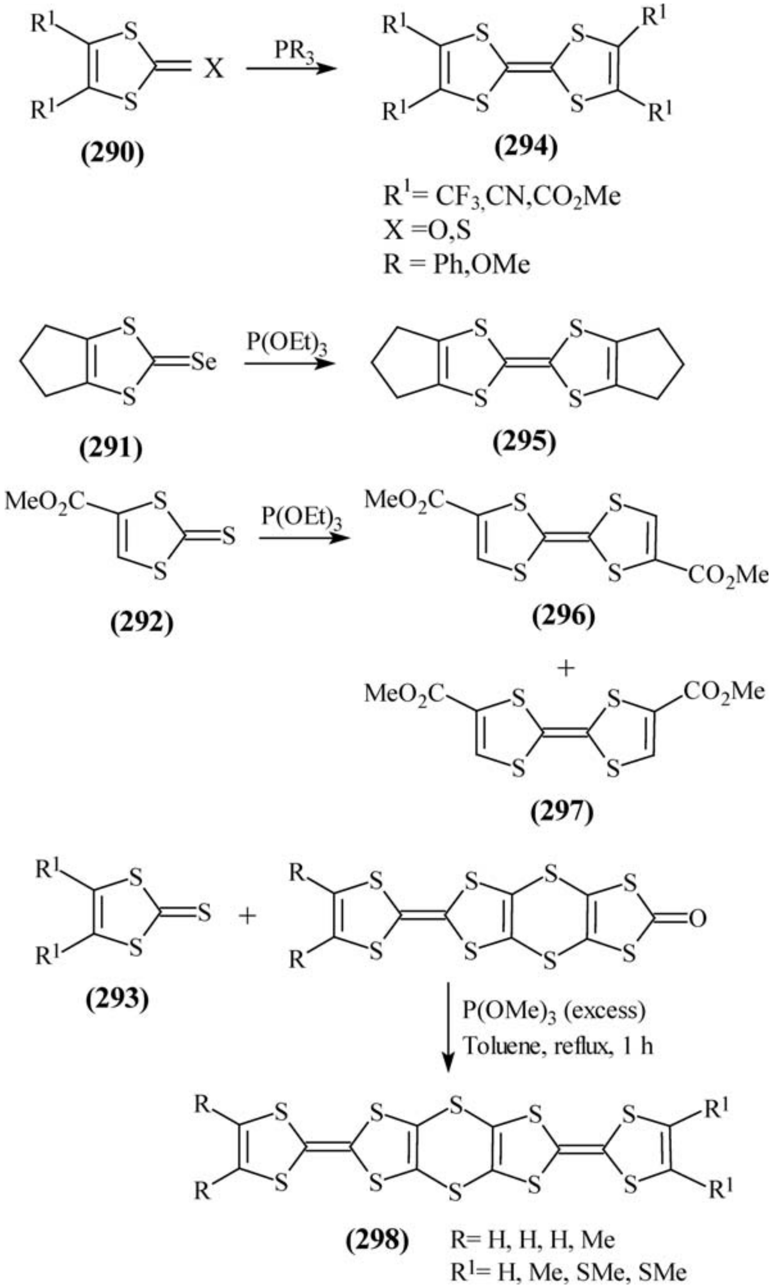
Efficient procedures utilizing the phosphonate method were described for the synthesis of unsymmetrically TTF derivatives[82–84] (302,305,308,310) (Scheme 33).

The quinonoid product (**311**) when reacted with cyclopentadiene gave the quinone derivative (**312**). The product (**314**) was obtained on reacting (**312**) with (**313**). The following $P(OMe)_3$ self-coupling reaction of thione (**314**) gave the expected precursor (**315**)[85] (Scheme 34).

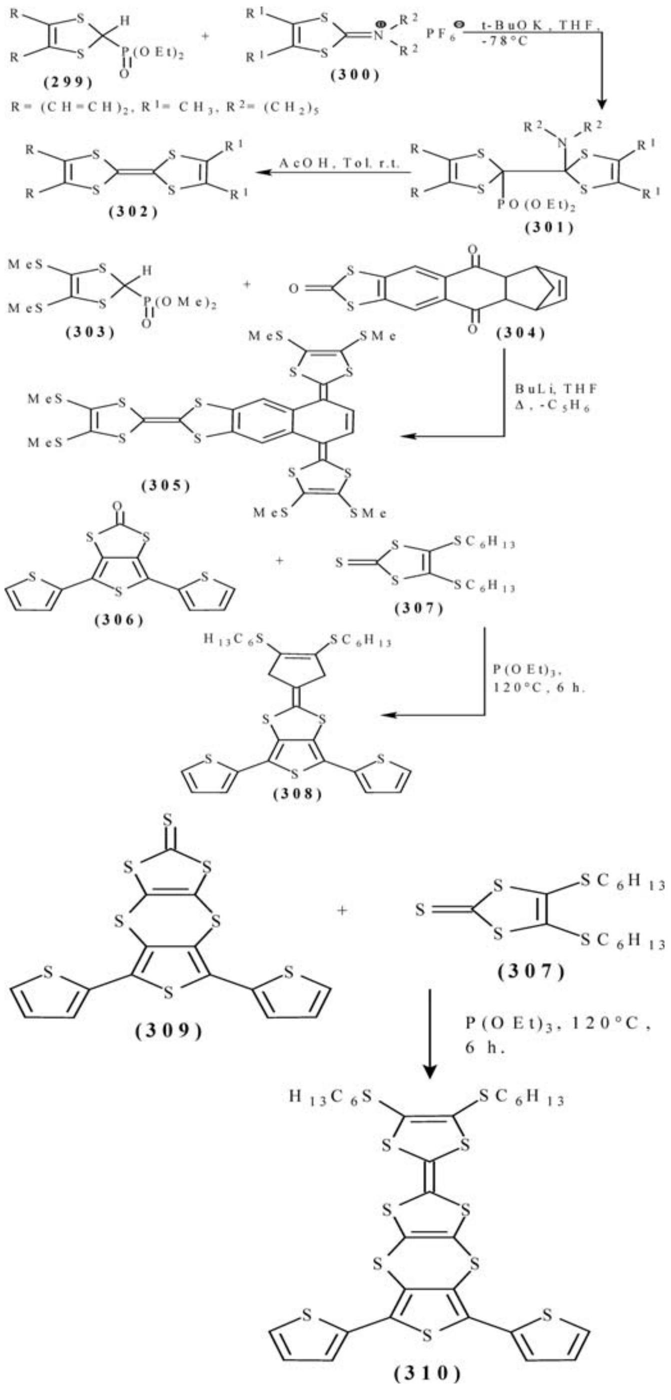
Desulfurization of (**316**) gave the diones (**317**), which are coupled to give TTF (**318**). Base opening action of the dithiolone rings of (**318**) followed by alkylation gives the novel per(alkylthio)dibenzo-TTF (**319**).[86]

The trithione (**320**) was introduced for the synthesis of several TTF derivatives. The effect of some reagents on (**320**) resulted in the formation of title compounds of the type (**321–324**)[87] (Scheme 35).

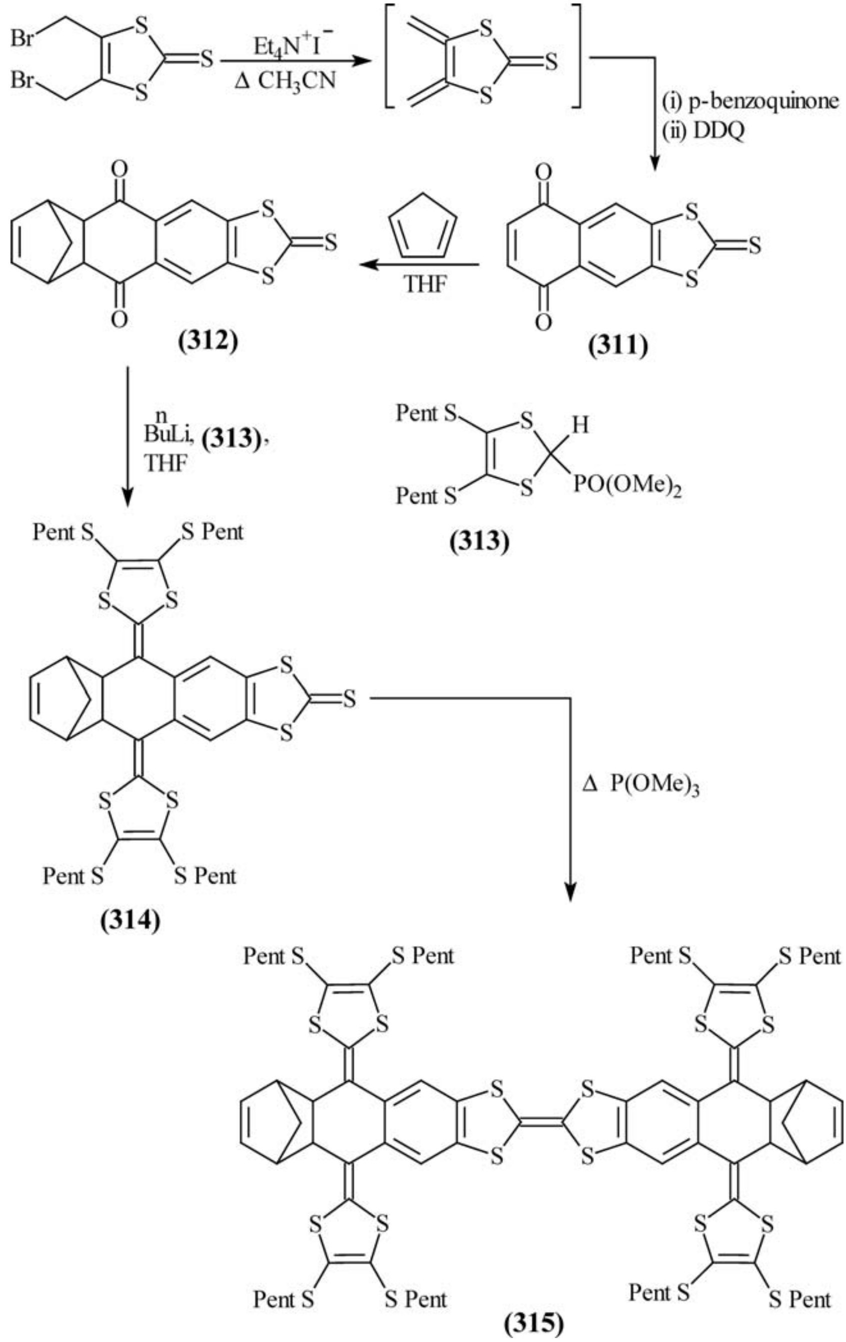
The syntheses of TTF family having a half moiety of bis(ethylenedithio)-TTF (BEDT-TTF) and a half moiety of TTF substituted with one (or two) hydroxymethyl group(s) are shown in (Scheme 36).[88] For the synthesis of (**328**), the two hydroxymethyl groups were introduced through reduction of the two aldehyde groups of (**327**) using $NaBH_4$. Therefore, a disymmetrical coupling between 1,3-dithiole-2-thiones (**325**) and (**220**) was used[88] (Scheme 36).


(290)
PR3
(294)
R1 = CF3, CN, CO2Me
X = O, S
R = Ph, OMe
(291)
P(OEt)3
(295)
(292)
P(OEt)3
(296)
(297)
(293)
P(OMe)3 (excess)
Toluene, reflux, 1 h
(298)
R = H, H, H, Me
R1 = H, Me, SMe, SMe

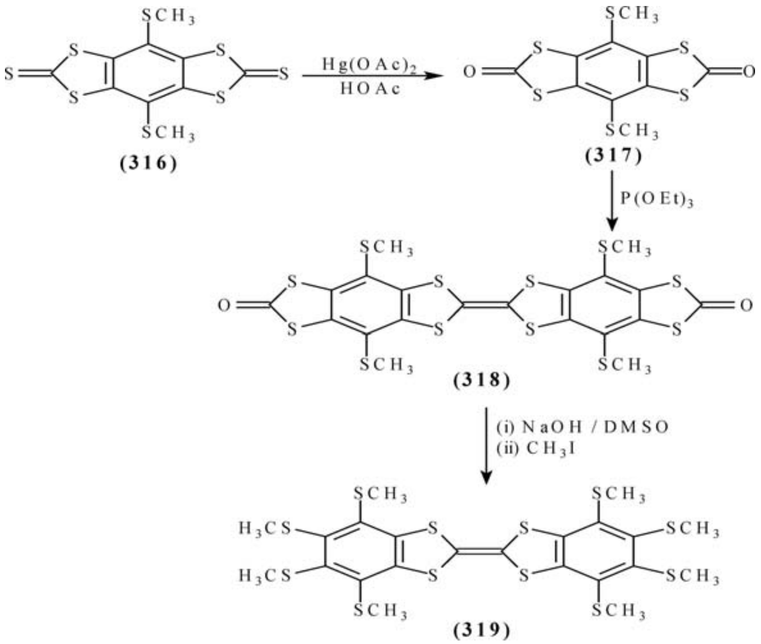
SCHEME 32

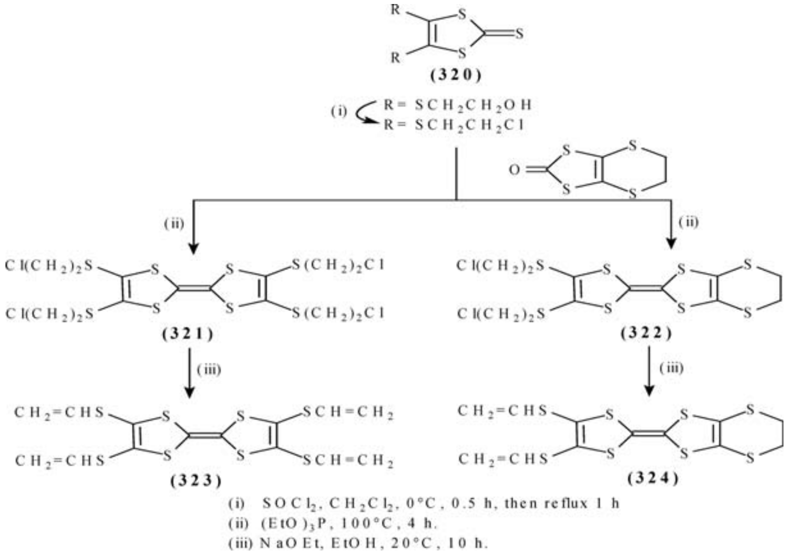

(299)
(300)
t-BuOK, THF, -78°C
R = (CH=CH)₂, R¹ = CH₃, R² = (CH₂)₅
(301)
AcOH, Tol. r.t.
(302)
(303)
(304)
BuLi, THF
Δ, -C₅H₆
(305)
(306)
(307)
P(OEt)₃, 120°C, 6 h.
(308)
(309)
(307)
P(OEt)₃, 120°C, 6 h.
(310)

SCHEME 33


Br
Br
S
S
S
$Et_4N^+I^-$
Δ CH_3CN
S
S
S
(i) p-benzoquinone
(ii) DDQ
O
O
S
S
S
THF
O
O
S
S
S
(312)
(311)
^{n}BuLi, (313),
THF
Pent S
Pent S
S
S
H
$PO(OMe)_2$
(313)
Pent S
S Pent
S
S
S
S
S
S
S
Pent S
S Pent
(314)
Δ $P(OMe)_3$
Pent S
S Pent
Pent S
S Pent
S
S
S
S
S
S
S
S
S
S
S
S
S
S
S
S
Pent S
S Pent
Pent S
S Pent
(315)

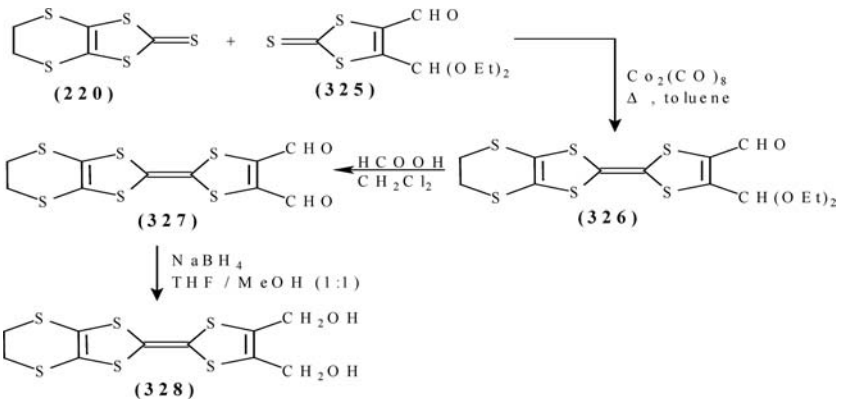
SCHEME 34





(i) $SOCl_2$, CH_2Cl_2, 0°C, 0.5 h, then reflux 1 h
(ii) $(EtO)_3P$, 100°C, 4 h.
(iii) NaOEt, EtOH, 20°C, 10 h.

SCHEME 35



SCHEME 36

Moreover, the synthesis of BEDT-TTF derivatives fused with heterocycles (**332**), (**334**) and (**337**) has been accomplished via BF_3-promoted reaction of organotin thiolates (**329**) with electrophiles (**330**)[89] (Scheme 37).

Diel's Alder cycloaddition reaction (2+4) was introduced for obtaining fused systems of the type (**340**) and (**343**) on the reaction of (**338**) with either (**339**) or (**341**)[90] (Scheme 38).

The conducting cation radical salts obtained from ET and the bis(areno)-fused derivatives (**340**) and (**343**) with gradually increasing and well-defined molecular dimensions, could find application as "molecular ruler" calibration standards in STM-based micromachining.

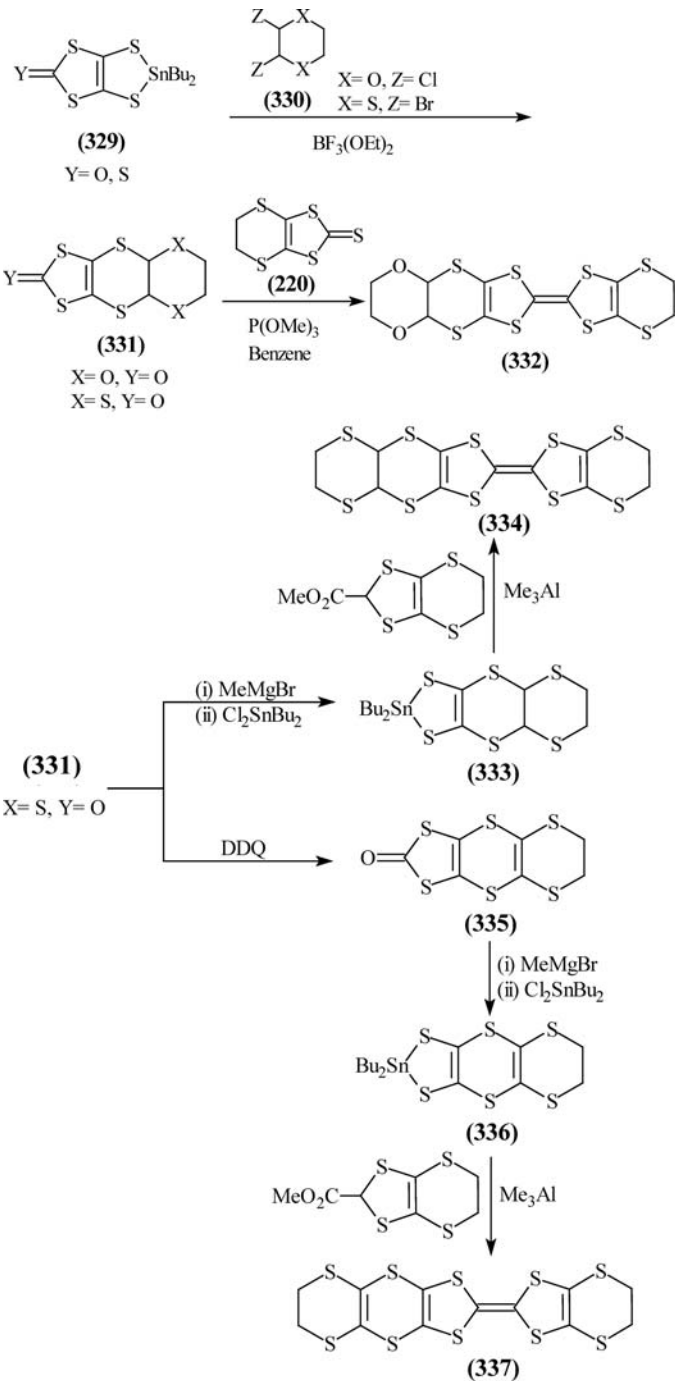
The unsymmetrically substituted TTF(s) and the subsequent transformation into a donor-σ-acceptor system is reported,[91] e.g., (**344**) and (**345**). The synthetic procedures for the synthesis of the target molecule (**353**) are illustrated in Scheme 39.

Novel tetrathiafulvaleno phanes, in which two TTFs are linked in a Criss Cross-overlapped arrangement by four methylene dithio bridges[92] has been synthesized[92] (Scheme 40).

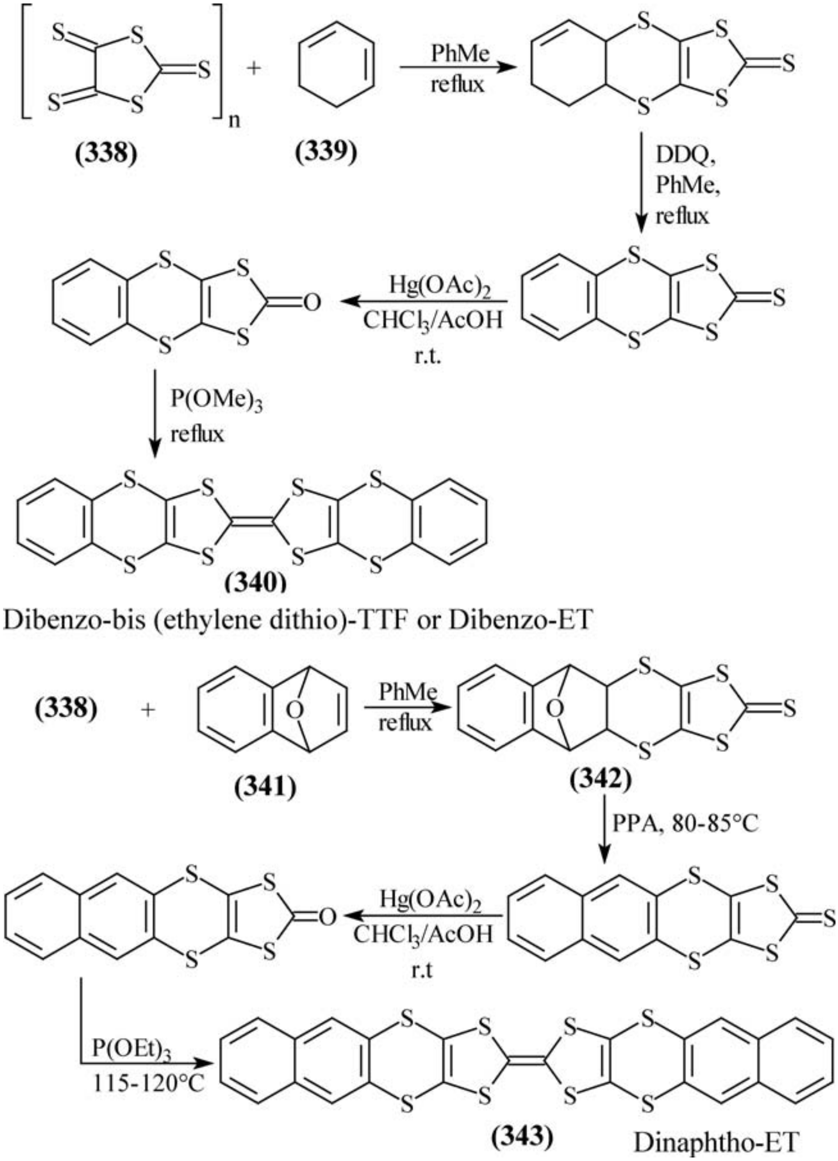
Recently, a series of thiophene-substituted TTF electron donors (**363**) has been prepared as shown in Scheme 41.[93]

The multistage synthesis of TTF derivatives (**368a–c**) containing the diacetylene group was carried out as shown in Scheme 42.[94]

Radical-cation salts based on TTF(s)-DHTTF (dihydrotetrathiafulvalene) fused donors (**371**) have been synthesized through the reaction of (**369**) with (**370**)[95] (Scheme 43).


(329)
Y= O, S
(330)
X= O, Z= Cl
X= S, Z= Br
BF3(OEt)2
(331)
X= O, Y= O
X= S, Y= O
(220)
P(OMe)3
Benzene
(332)
(334)
Me3Al
MeO2C
(i) MeMgBr
(ii) Cl2SnBu2
Bu2Sn
(333)
(331)
X= S, Y= O
DDQ
(335)
(i) MeMgBr
(ii) Cl2SnBu2
(336)
Me3Al
MeO2C
(337)

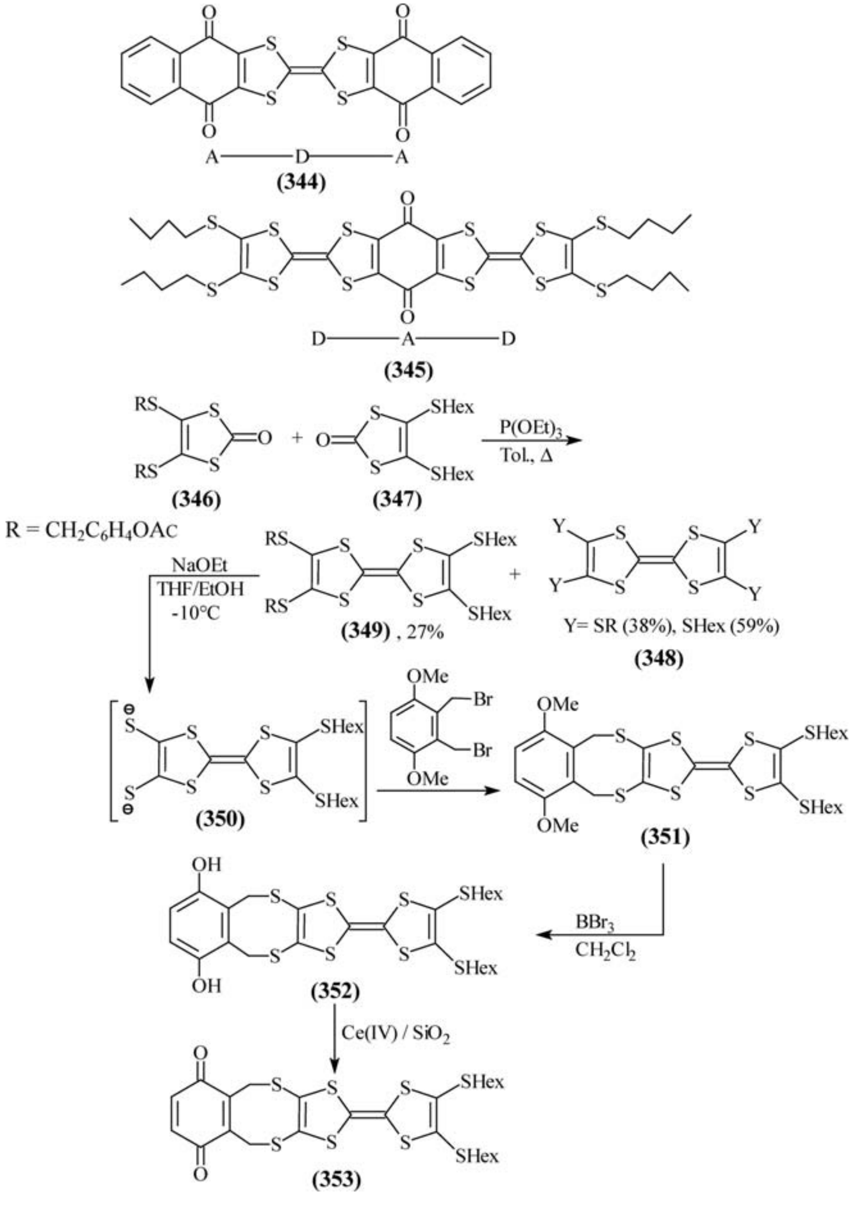
SCHEME 37



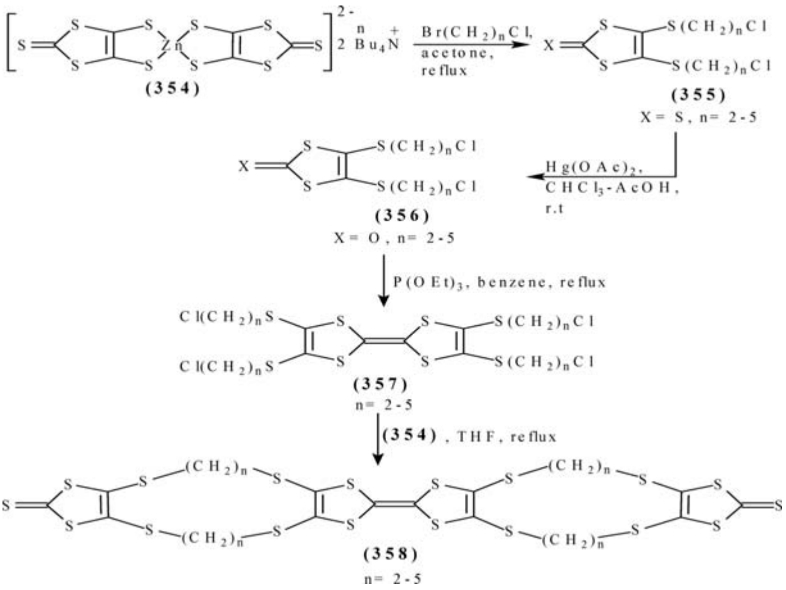
SCHEME 38

1,3,4,6-Tetrathiapentalene-2,5-dione (**73**) is considered a versatile precursor for synthesis of TTF derivatives.

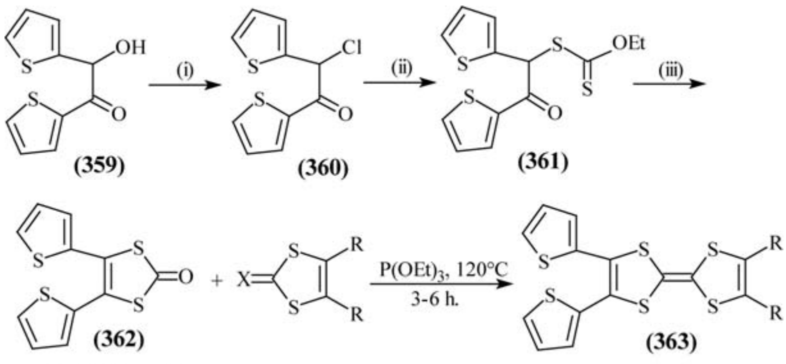
Starting from (73) or (174), TTF derivatives (**373a**,**b**)[96] could be obtained (Scheme 44).[96]


A—D—A
(344)
D—A—D
(345)
RS
(346)
(347)
SHex
P(OEt)$_3$
Tol., Δ
R = CH$_2$C$_6$H$_4$OAc
NaOEt
THF/EtOH
-10°C
(349), 27%
Y= SR (38%), SHex (59%)
(348)
OMe
Br
(350)
(351)
BBr$_3$
CH$_2$Cl$_2$
OH
(352)
Ce(IV) / SiO$_2$
(353)

SCHEME 39



SCHEME 40

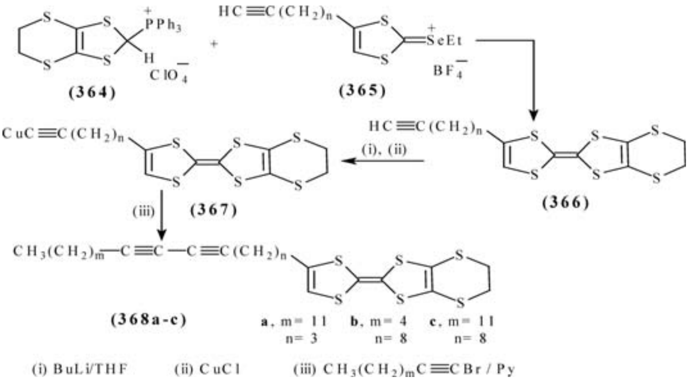


a, R= 2-Thieny, X= O
b, R= H, X= S
c, R= $S(CH_2)_2CN$, X= S
d, R-R= $-S(CH_2)_2S-$, X= S

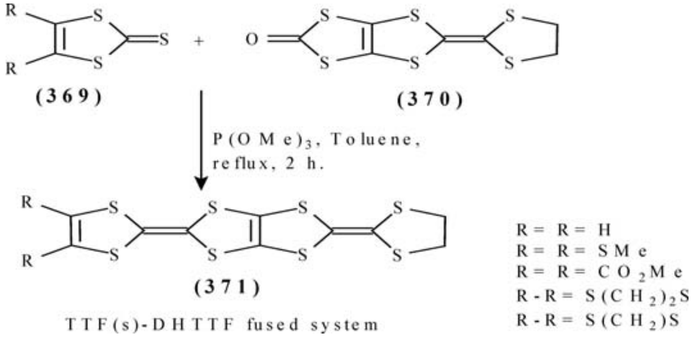
R= 2-Thienyl, H, $-S(CH_2)_2CN$,
R-R= $-S(CH_2)_2S-$

(i) PPh_3, CH_2Cl_2/CCl_4 (1:2), r.t, 24 h.
(ii) KSC(S)OEt, Me_2CO, r.t, 15 min.
(iii) HBr/AcOH, r.t, 1 h.

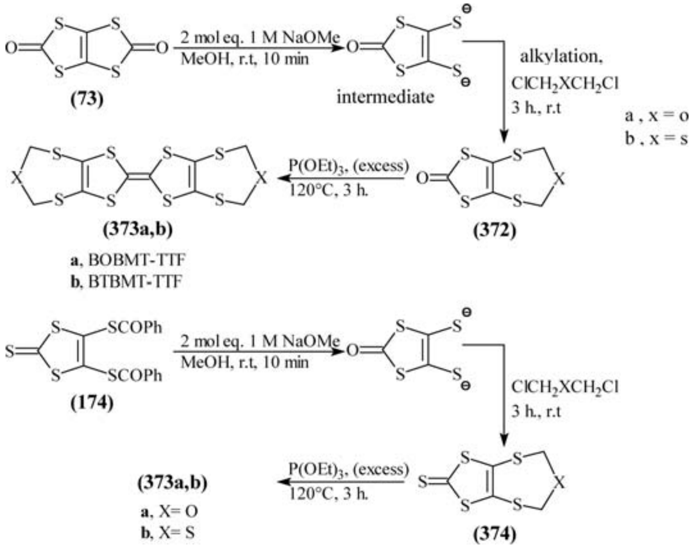
SCHEME 41



SCHEME 42

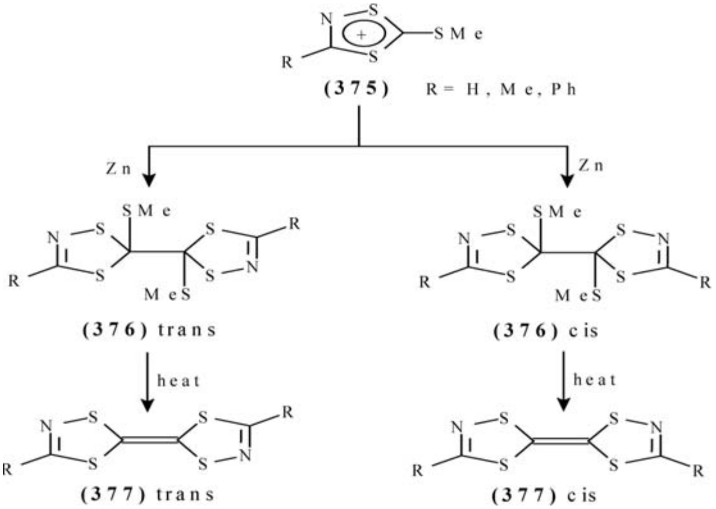


SCHEME 43



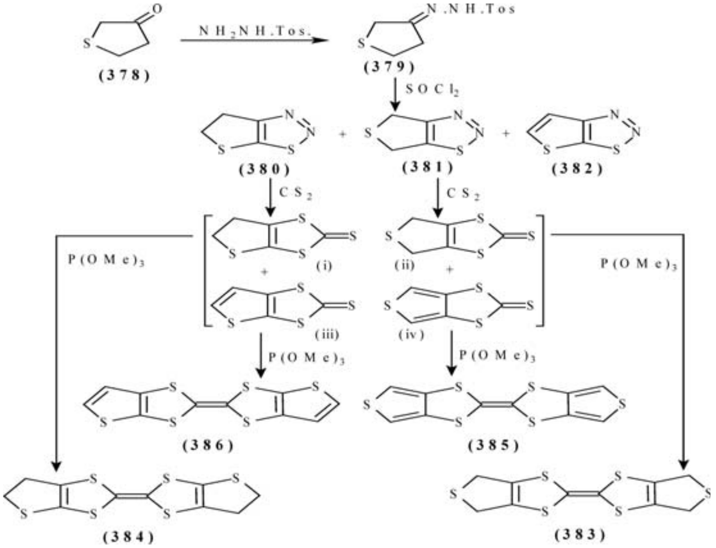
SCHEME 44

Reduction of (**375**) with zinc powder yields the corresponding diazahexathioorthooxalate derivatives (**376**). Thermolysis of (**376**) in the presence of catalytic iodine affords the tetrathiadiazafulvalenes (**377**)[97] (Scheme 45).



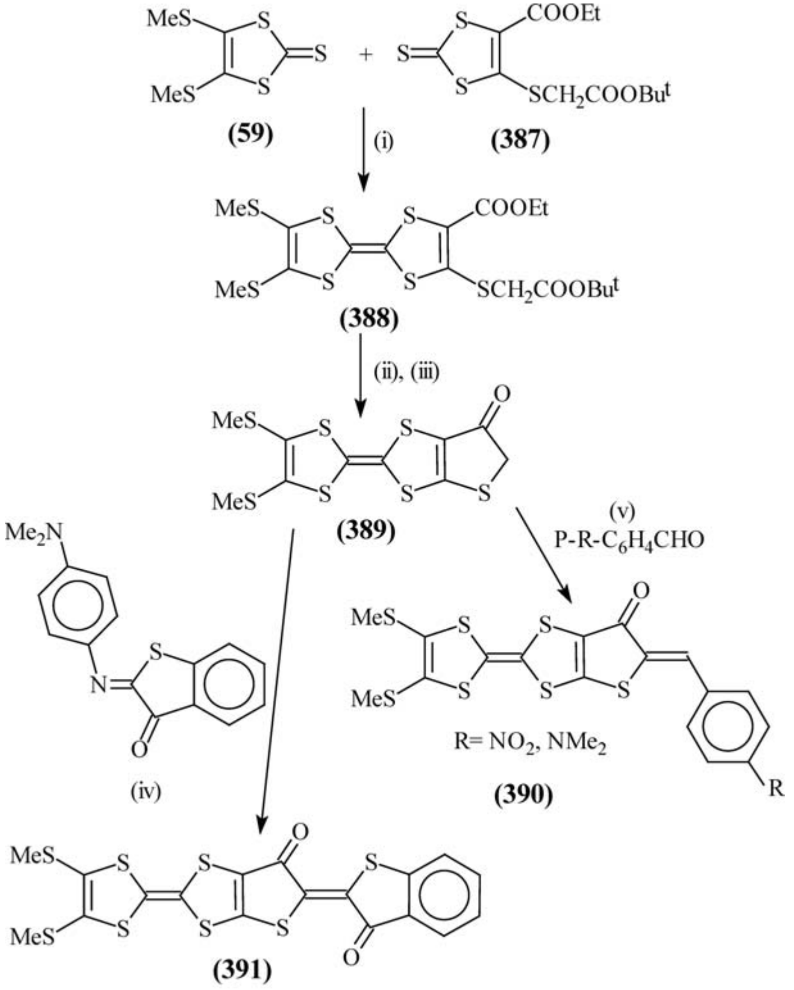
SCHEME 45

Reaction of the hydrazone derivative (**379**) with $SOCl_2$ formed a mixture of (**380–382**). On reaction with carbon disulfide, compounds (**385**) and (**386**) were formed via the intermediates (i-iv)[98] (Scheme 46).



SCHEME 46

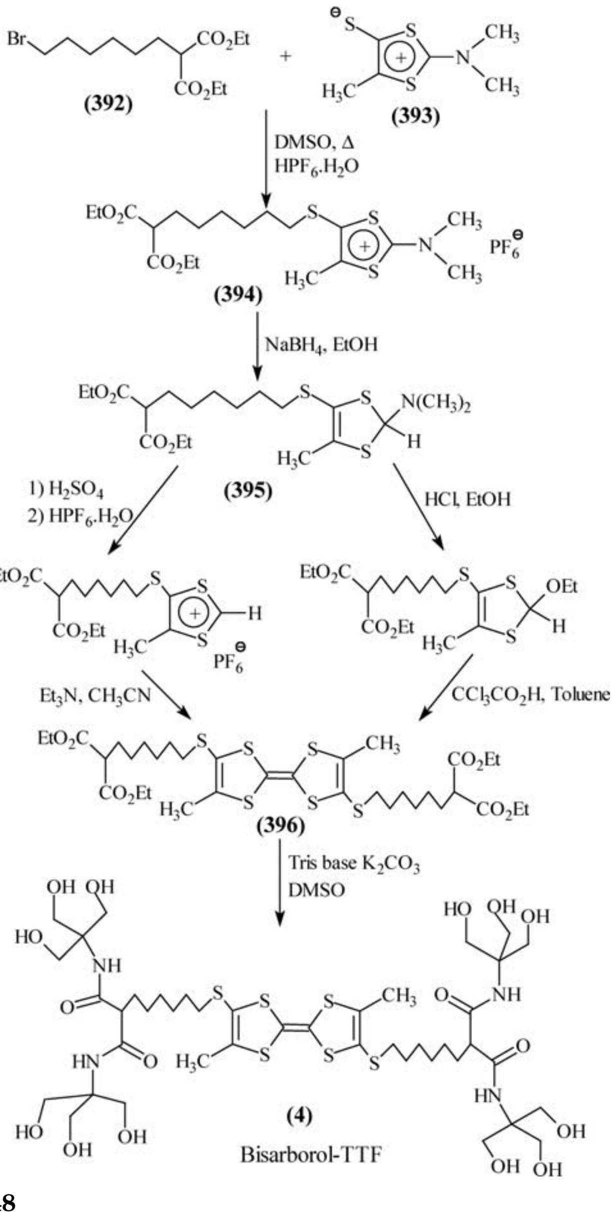
The synthesis of a hybrid molecule involving both TTF and thioindigo moieties was reported.[99] The synthetic strategy is outlined in Scheme 47.



(i) $P(OEt)_3$, reflux, 15 min.
(ii) t-BuOK / t-BuOH, 45 min.
(iii) CF_3COOH / AcOH, 70°C, 30 min.
(iv) AcOH, reflux, 45 min.
(v) AcOH, 30 min.

SCHEME 47

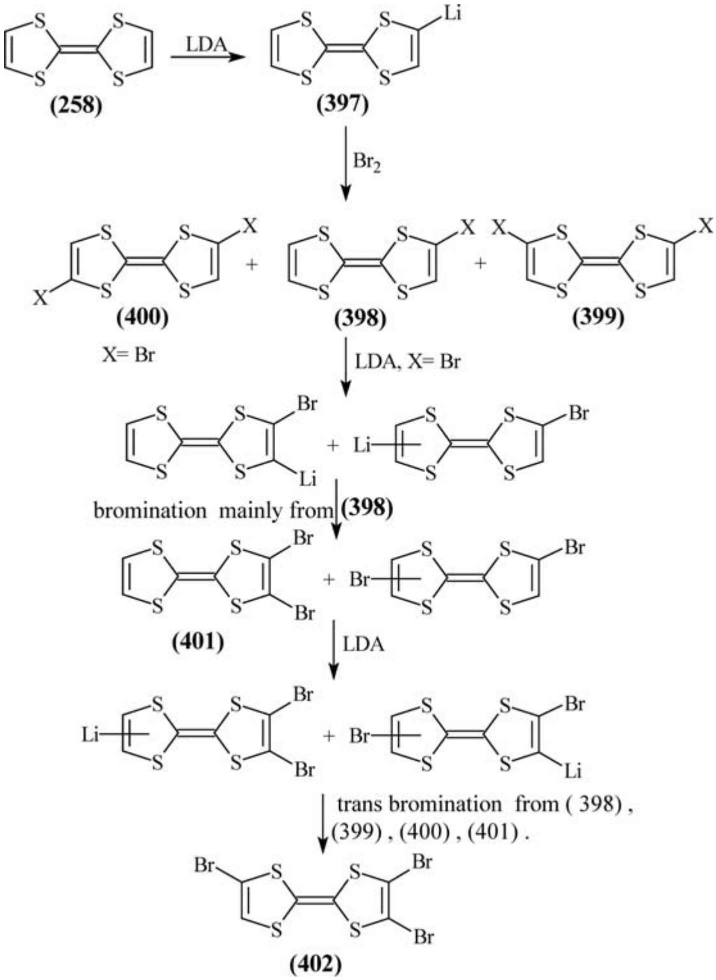
Mesoion (**393**) was S-alkylated with the bromodiester (**392**) yielding the dithiolium salt (**394**). Reduction of (**394**) with sodium boro hydride produced the dithiole derivative (**395**). Following subsequent reactions, the final product (**4**) was obtained[100] (Scheme 48).



SCHEME 48

(B) Reactions of Tetrathiafulvalenes

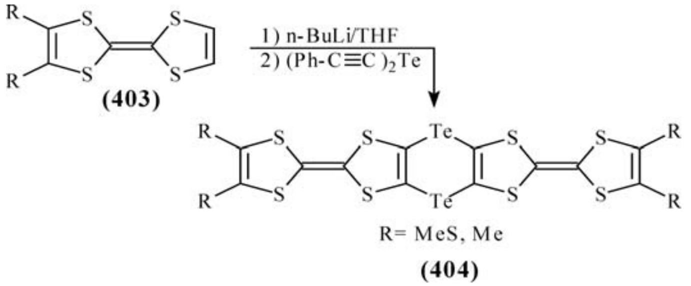
A halogeno derivatives of TTF(s) were introduced in chemistry via lithiation of TTF (**258**) with lithium diisopropylamide (LDA) followed by treating with halogenating agents (Scheme 49).[101]



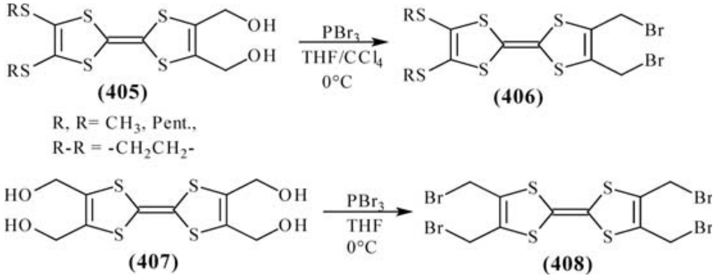
SCHEME 49

Dimeric TTF containing covalent bridges were synthesized for improving electrical conductivity and superconductivity.

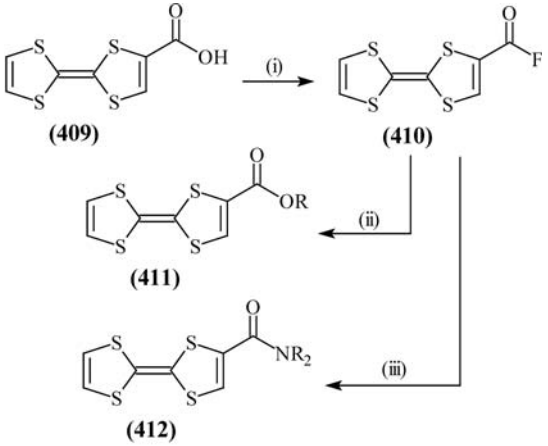
A new molecular donor composed of two TTF moieties fused to 1,4-ditellurin (**404**) has been synthesized[102] via lithiation of (**403**) followed by reaction with alkynyle tellurides.



Efficient synthesis of novel halogenated TTF derivatives (**406**,**408**) were generated via replacement of hydroxyl groups in (**405**,**407**) with bromine.[103]



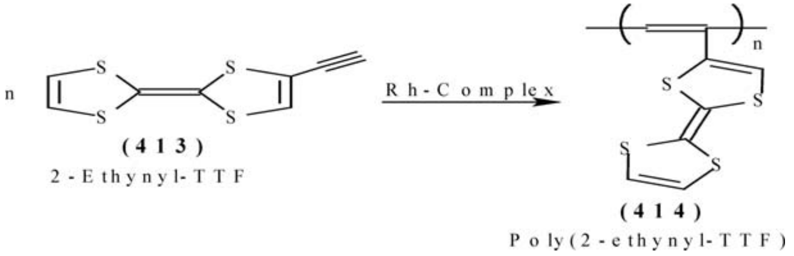
Fluorocarbonyl TTF (**410**) has been synthesized under mild conditions. Reaction of (**410**) with alcohols and amides furnished formation of esters and amides in quantitative yield[104] (Scheme 50).



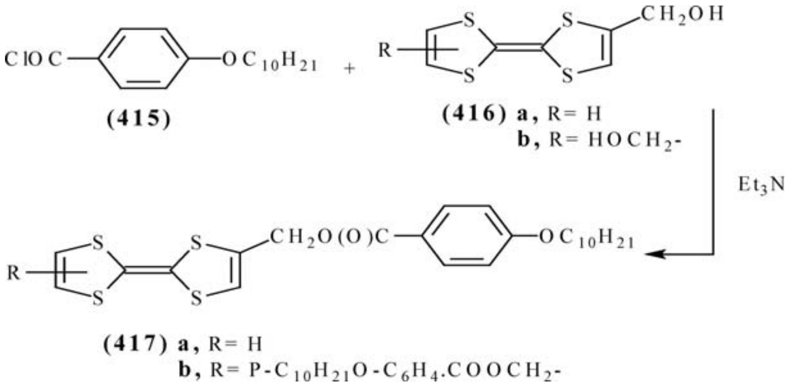
(i) Cyanuric fluoride, pyridine, CH_2Cl_2
(ii) ROH, DMAP [4-(dimethylamino)-pyridine]
(iii) R_2NH

SCHEME 50

Polymerization of 2-ethynyl-TTF (**413**) was carried out under the effect of $[Rh(\mu\text{-}Cl)(\eta^4\text{-nbd})]_2$ (nbd = norbornadiene) to give (**414**). This catalyst is known as an active catalyst for polymerization of arylacetylenes.[105]

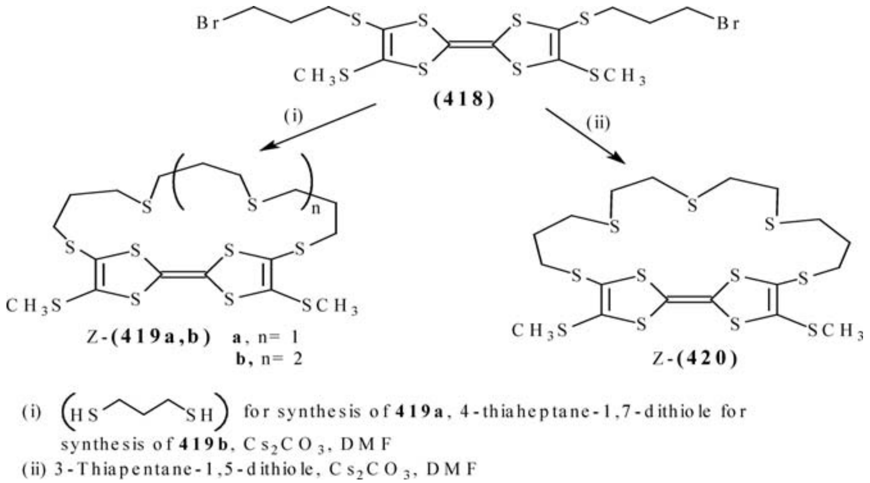


Acid chloride (**415**) was reacted with alcohols (**416a**,**b**) to give the corresponding esters (**417a**,**b**).[106]



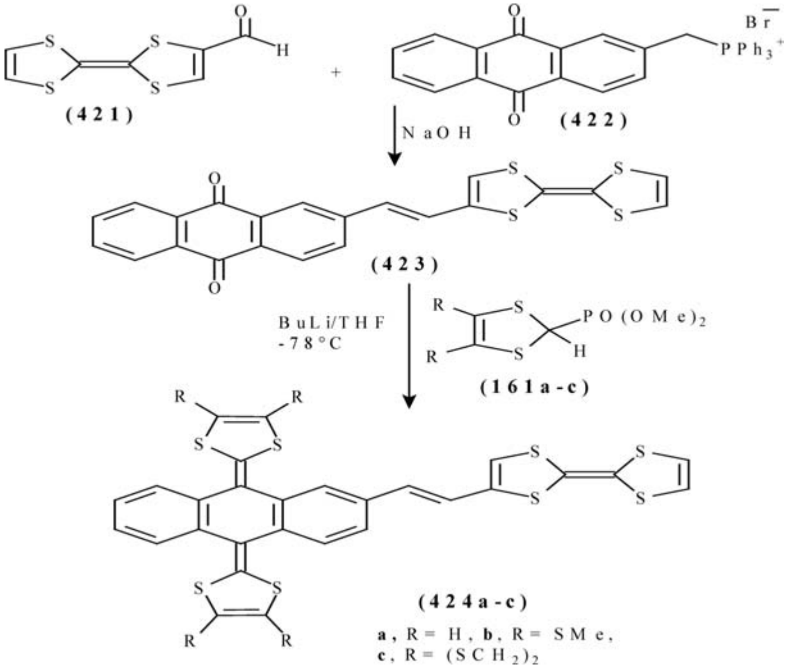
Thiacrown ether TTF derivatives (**419a**,**b** and **420**) were synthesized for using it as redox responsive ligands. Reaction of TTF haloderivatives (**418**) with thiols produced the required products (**419a**,**b**) and (**420**) in the form of Z-isomers.[107]

New hybrid TTF dimers (**424a–c**) have been prepared by a Wittig-Horner method. 2-(Tetrathiafulvalenylvinyl)-9,10-anthraquinone (**423**) was obtained on reacting (**421**) with the quinone (**422**). On subjecting (**423**) to the reagents (**161a–c**), the stable charge-transfer products (**424a–c**) were obtained[108] (Scheme 51).

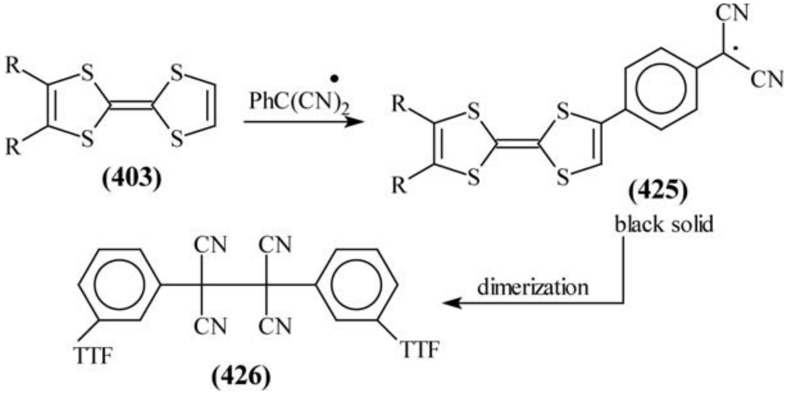


(i) for synthesis of **419a**, 4-thiaheptane-1,7-dithiole for synthesis of **419b**, Cs_2CO_3, DMF
(ii) 3-Thiapentane-1,5-dithiole, Cs_2CO_3, DMF

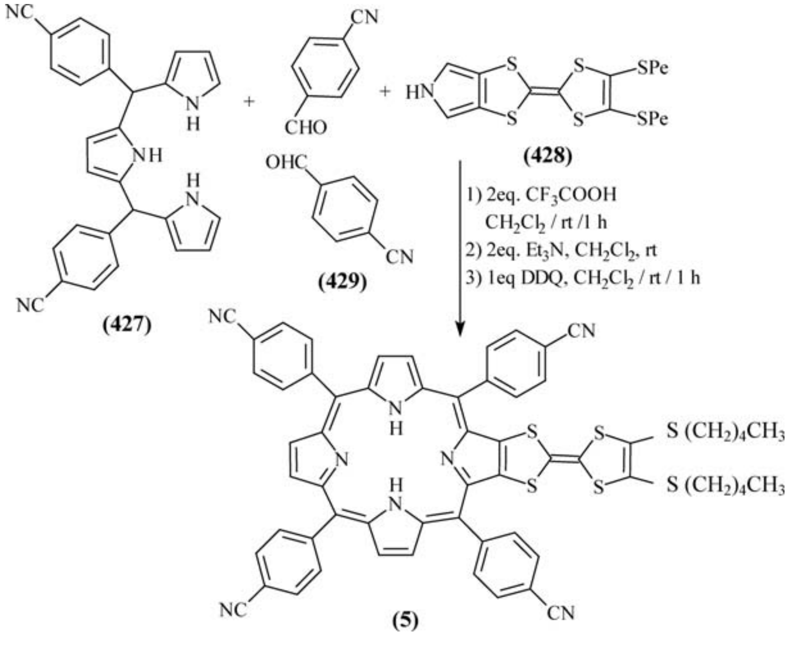
Synthesis of the electron rich skeleton having donating property (**426**) was successful. Treating TTF (**403**) with phenyldicyano methyl anion resulted in the formation of a black solid product that was identified as (**425**). Dimerization of (**425**) gave (**426**).[109]



SCHEME 51

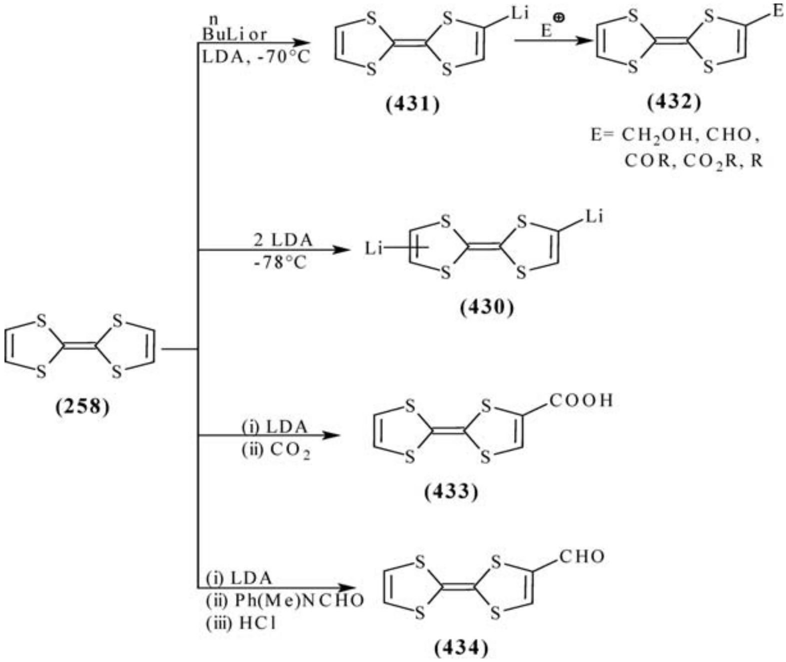


Porphyrin (**5**) was prepared via reaction a mixture of (**427**), (**428**) and aldehydes (**429**) in trifluoroacetic acid[16] (Scheme 52).



SCHEME 52

Lithiation of TTF (**258**) has been accomplished at -78°C by either lithium diisopropylamide or by n-butyllithium. 1-Lithio-TTF (**431**) reacts at −70°C with a series of electrophiles to afford the corresponding alcohols, aldehydes, ketones, carboxylic acids and esters, as well as mono-alkylated TTFs. Improvement of this procedure allowed the synthesis of carboxy-TTF (**433**) and formyl-TTF (**434**). The high yield preparation of these compounds makes them attractive building blocks for redox systems[110] (Scheme 53).

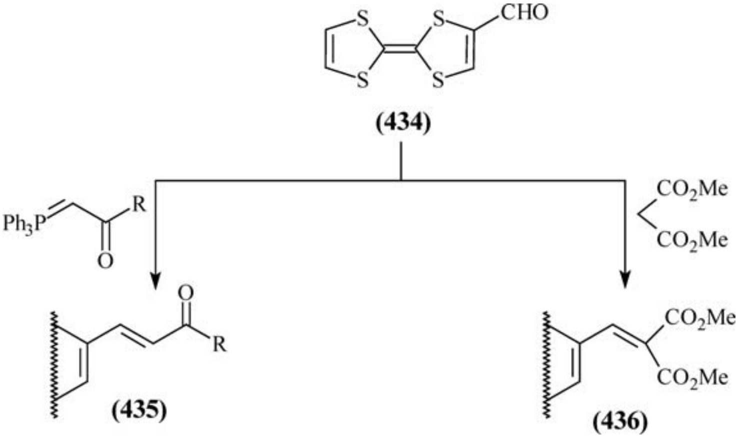


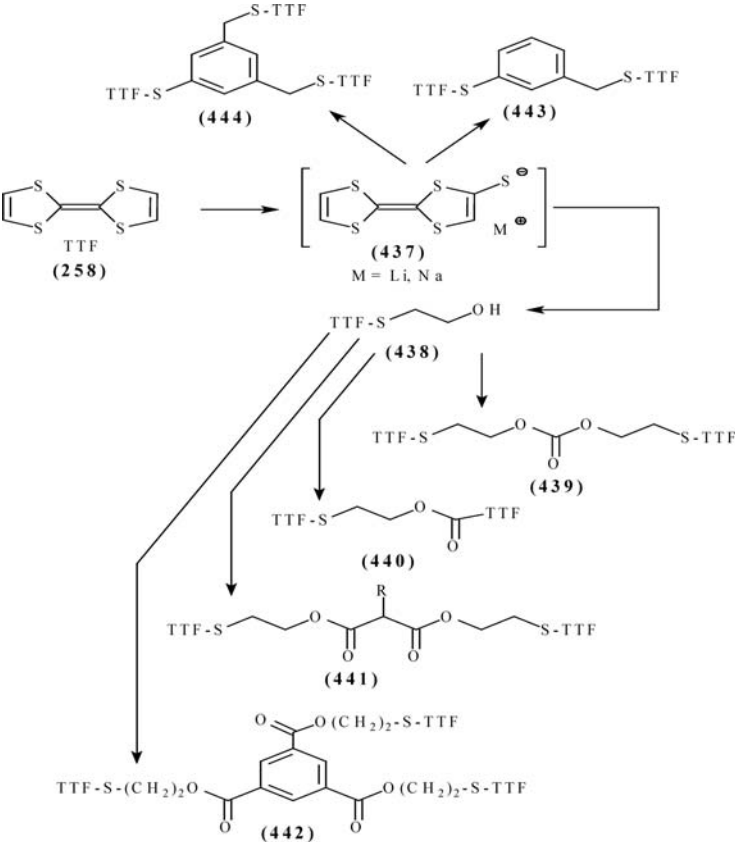
SCHEME 53

Wittig alkenation of formyl-TTF (**434**) with resonance stabilized ylides afforded chain elongated alkenes (**435**) in high yields, whereas, Knoevenagel-type condensation gave the corresponding 1,1-bis (carboxymethyoxy)ethene derivative (**436**) in only 10% yield.[110]

For the formation of conducting charge-transfer complexes, new bis- and tris-TTF derivatives have been prepared. The TTF-thiolate anion (**437**) reacts with 2-bromoethanol to yield alcohol (**438**) from which the bis- and tris-TTF systems (**439–442**) have been obtained.

Thiolate anion (**437**) reacts with bis- and tris-bromomethylbenzene, to give bis- and tris-TTF derivatives (**443**) and (**444**), respectively[111] (Scheme 54).


CHO
(434)
Ph_3P
R
O
CO_2Me
CO_2Me
O
R
(435)
CO_2Me
CO_2Me
(436)


S-TTF
TTF-S
S-TTF
(444)
TTF-S
S-TTF
(443)
TTF
(258)
(437)
M = Li, Na
TTF-S
OH
(438)
TTF-S
O
O
S-TTF
O
(439)
TTF-S
O
TTF
O
(440)
R
TTF-S
O
O
S-TTF
O
O
(441)
O
$O(CH_2)_2$-S-TTF
TTF-S-$(CH_2)_2O$
$O(CH_2)_2$-S-TTF
O
O
(442)

SCHEME 54

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