Synthesis Strategies and Chemistry of Nonsymmetrically Substituted Tetrachalcogenafulvalenes

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Contents

1. Introduction

Interest in the chemistry of tetrathiafulvalene (TTF)[1] was born with the discovery in 1973 of the first organic metal, TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane).[2] A few years later, this interest increased considerably with the discovery of superconducting salts[3−6] based on TTF derivatives such as TMTSF (tetramethyltetrathiafulvalene),[7] BEDT-TTF (bisethylenedithiotetrathiafulvalene),[8−10] or DMET (dimethyldiselenaethylenedithiodithiafulvalene)[11] (Scheme 1).

Since then, the progress made in the synthesis of such molecules[12−20] has been closely related to the discovery of new materials[21] exhibiting conducting,[22−27] superconducting,[28,29] magnetic,[30−32] and optical properties.[33−35] More recently the increasing search for solids displaying combined physical properties[36−41]

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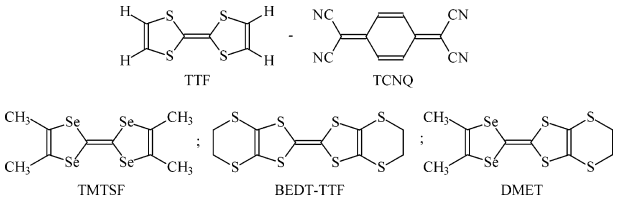
Jean-Marc Fabre was born at Nimes (France) in 1943. He carried out graduate work at the University of Montpellier (France) and then worked at Mobil Oil while finishing his doctoral thesis on the stereochemistry of organic reactions leading to functionalized carbocycles. In 1973 he began working on the chemistry of TTF and of organic conductors and superconductors. As Visiting Professor (1985–1986) at the University of Virginia, he worked with Professor B. A. Averill on the intercalation chemistry of TSF derivatives. He became Full Professor in 1985 and continued research in the fields of organic materials and of the chemistry of TTF derivatives at the University of Montpellier and then (1998) at ENSCM (UMR 5076, Montpellier), where he works today.

Scheme 1



and in the construction of supramolecular architectures[42−50] such as oligomers,[51−55] dendrimers,[14,56−59] macrocycles,[60−64] and cyclophanes[65−67] derived from TTF is largely responsible for the developments underway today in the chemistry of these tetrachalcogenated compounds and, more particularly, of their nonsymmetrical derivatives that are the most frequently involved in the numerous investigations mentioned above. The preparation of these dissymmetric derivatives is primarily carried out using three strategies, as mentioned by Krief[16] (Scheme 2): strategy I, based on the double condensation of dichalcogenolate entities with tetrachloroethylene; strategy II, which corresponds to the monocondensation of two 1,3-dichalcogenole rings; and strategy III, which consists of the replacement of one (or several) hydro-

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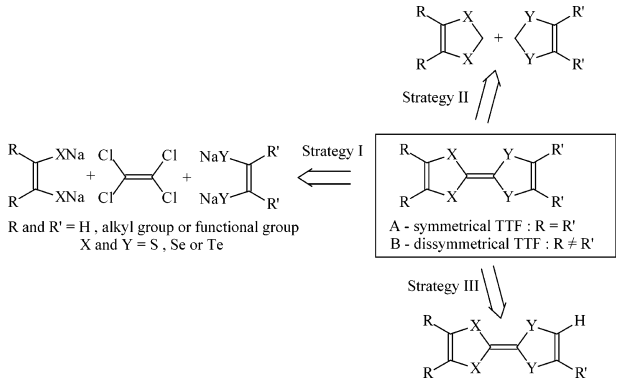
Scheme 2



gen atom(s) in TTF or TSF (tetraselenafulvalene), in particular by a substituent (R = alkyl chalcogenoalkyl functional group).

Unfortunately, some of these approaches quickly show their limits, since they give mixtures of symmetric (A)[1] and dissymmetric (B)[16] TTFs (Scheme 2). To circumvent these difficulties, a certain number of methods of synthesis presenting different degrees of selectivity[16−20] have been proposed. As will be seen hereafter, they mainly derive from strategy II and involve Wittig, Horner−Wadsworth−Emmons, and organometallic type condensations.

The objective of this article is to present each one of these strategies and the related synthetic methods through relevant examples, to describe the fundamental mechanism involved, when possible, and to point out their advantages, and disadvantages, and the potential for their future development. This article also aims to establish the respective importance of their current use with the help of some recent examples taken from the literature. By selected typical examples, we show how chemical modifications at the periphery of the TTF molecule such as metalation and functionalization allow the transformation of organic functions, the introduction of specific groups, or the construction of more complex architectures according to needs.

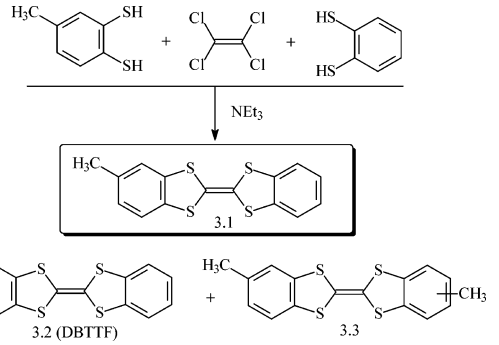
2. Strategy I: Biscondensation of 1,2-Dichalcogenolates with Tetrachloroethylene

This strategy for synthesis of a TTF is the oldest. It made possible the preparation in 1926 of dibenzotetrathiafulvalene (DBTTF) by condensation of *o*-dithiolbenzene with tetrachloroethylene[68] in a basic medium. Reused in the seventies, this method enabled the nonselective synthesis (Scheme 3) of the dissymmetric TTF **3.1** in poor yield (15%) after separation of the symmetrical species **3.2** and **3.3** by repeated recrystallizations from pyridine.[69]

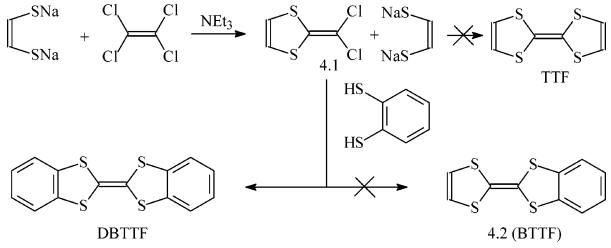
Unfortunately, this approach was then unsuccessfully attempted for the preparation of (Scheme 4) other dissymmetric TTF derivatives such as **4.2** and its dicyano analogue.[70] The failure is probably due to a transdithiolation of the dichloro intermediate **4.1** formed in such reactions.

Disadvantages and Advantages. Poor yield, nonselectivity, and the difficulty in obtaining a wide variety of ethylenic 1,2-dithiolates as starting compounds are the main drawbacks of this route, which

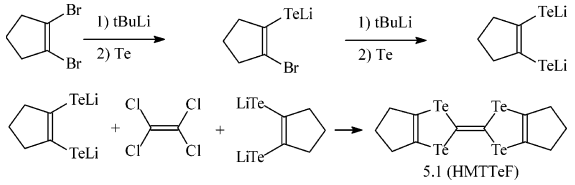
Scheme 3



Scheme 4



Scheme 5



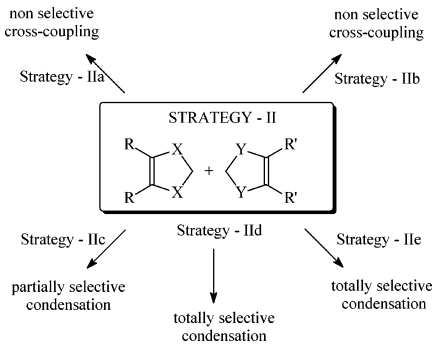
is no longer used today except to prepare tellurium derivatives of TTF[71] such as HMTTeF **5.1** (Scheme 5).[72]

3. Strategies II: Monocondensation of Two 1,3-Dichalcogenole Rings

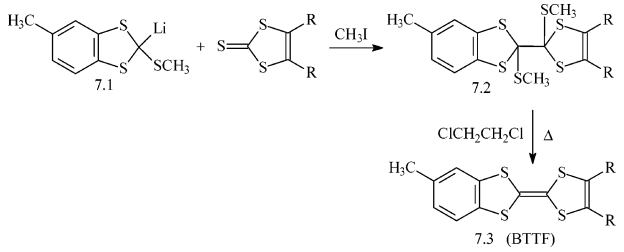
Strategies II for the synthesis of dissymmetric TTFs (Scheme 6) can be nonselective and lead to mixtures (strategies IIa and IIb) or, on the contrary, be partially or completely selective (strategies IIc, IId, and IIe).

Before examining these various approaches in detail, it is recalled that symmetric and dissymmetric tetrathiafulvalenes were obtained in good yields by condensation of two 1,3-dithiole rings via the pyrolysis of intermediate hexathioorthooxalates **7.2** (Scheme 7).[73,74]

Scheme 6



Scheme 7



Despite its interest, the use of this method has unfortunately remained restricted to the preparation of some benzo-TTF derivatives **7.3**, certainly due to the fact that only lithiated reagents **7.1** stabilized by a benzo group could be isolated up to now. Moreover, the reactivity of such metalated heterocyles seems to be very dependent on the nature of the medium.[75]

3.1. Nonselective Strategies: Cross-coupling Reactions

These nonselective strategies for the synthesis of dissymmetric TTFs are adaptations of the methods described in many review articles[1,16−20] for the preparation of symmetric TTFs. IIa corresponds to the condensation of 1,3-dithiolium salts in a basic medium, while IIb involves the coupling of 1,3-dichalcogenole-2-chalcogenones (also named 2-chalcoxo-1,3-dichalcogenoles) by the action of a trivalent phosphorus derivative (Scheme 8).

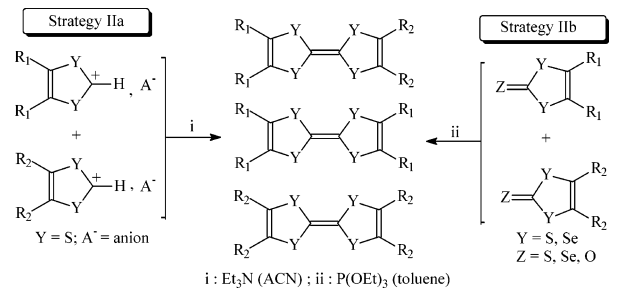
3.1.1. Strategy IIa: Cross-coupling of 1,3-Dithiolium Salts

The cross-coupling reaction of two dithiolium salts has been used since the early seventies[76−78] and is generally carried out in the presence of triethylamine.

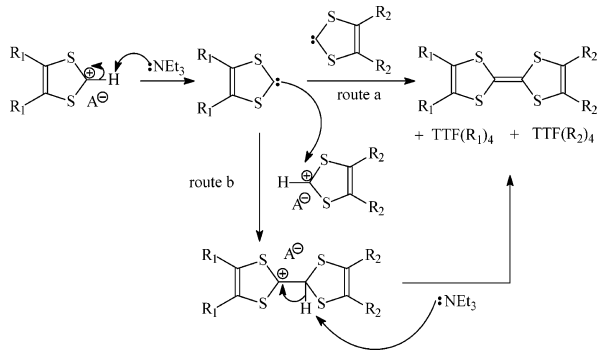
Mechanism. The mechanism[1,16] is suggested to proceed via the generation of a dithiolium carbene followed by dimerization with another carbene (route a) or followed by reaction with the dithiolium salt (route b) and subsequent deprotonation of the intermediate adduct (Scheme 9).

Disadvantages and Advantages. The principal disadvantage is the concomitant formation of the two symmetric byproducts, thus requiring chromatographic separation of the target compound. When the polarities of the three TTF molecules obtained as a mixture are too close, it is difficult to separate the desired nonsymmetric TTF, as shown by the low yield obtained in the synthesis of EDT-TTF (ethylenedithiotetrathiafulvalene) (18%) and of its dimethyl

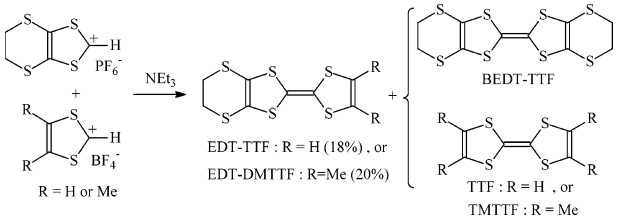
Scheme 8



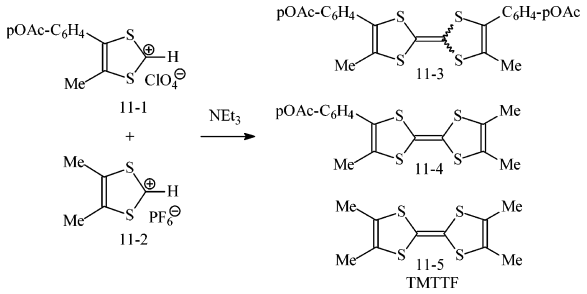
Scheme 9



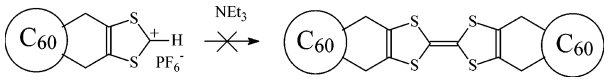
Scheme 10



Scheme 11



Scheme 12



analogue EDT-DMTTF (ethylenedithiodimethyltetrathiafulvalene) (20%) (Scheme 10).[79,80]

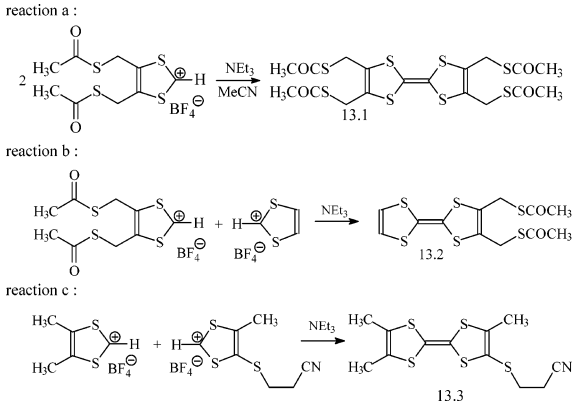
This difficulty is more marked when the reactivities of the two dithiolium salts used are quite different from each other. As shown in Scheme 11,[81] the functionalized nonsymmetric TTF **11.4** was obtained in only 15% yield whereas the symmetric TMTTF **11.5** was obtained as the major compound (31%), indicating the higher reactivity of the dimethyl-substituted dithiolium salt (**11.2)** in this case.

It was recently shown that in certain cases the dithiolium salt does not react and the condensation reaction fails (Scheme 12).[82]

It should finally be noted that this method is not applicable to air sensitive 1,3-diselenolium salts, which easily decompose in basic media to produce elemental selenium[16,83] in particular.

Recent Examples of the Use of Strategy IIa. Despite these disadvantages, this strategy is still occasionally employed to prepare (Scheme 13)[84] symmetric (**13.1**) and dissymmetric functionalized TTFs (**13.2**, **13.3**),[84,85] the two latter being successfully separated from the mixture by chromatography (Scheme 13c).

Scheme 13



3.1.2. Strategy IIb: Cross-coupling of 1,3-Dichalcogenole-2-chalcogenones

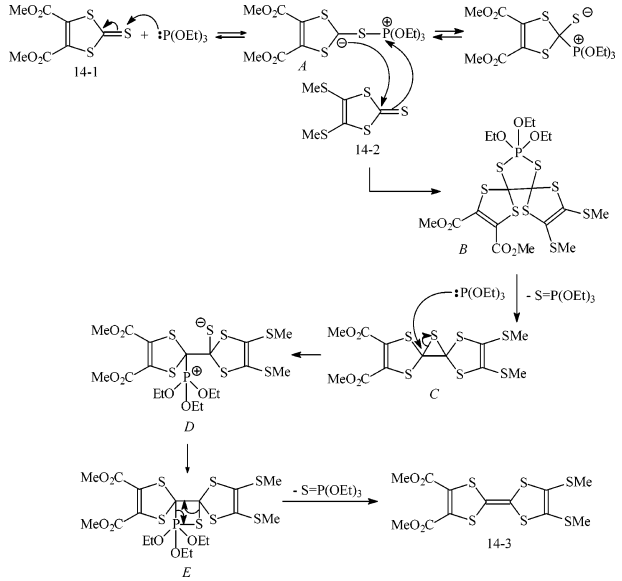
The cross-coupling of two 1,3-dichalcogenole-2-chalcogenones, first used in 1970 by Hartzler,[86] is based on the dechalcogenation of chalcogenones by the action of phosphine or, more efficiently, of phosphites.[16] It has been very largely used for the preparation of dissymmetric TTF[17−20] and also to build more complex structures such as quadruple-bridged bis-TTF[52] for example.

Mechanism. Several suggestions for the reaction mechanism have been made starting from specific cases.[87−89] The most recent arises from the study of the phosphite-mediated cross-coupling reaction of two different dithiole-thiones (Scheme 14):[90]

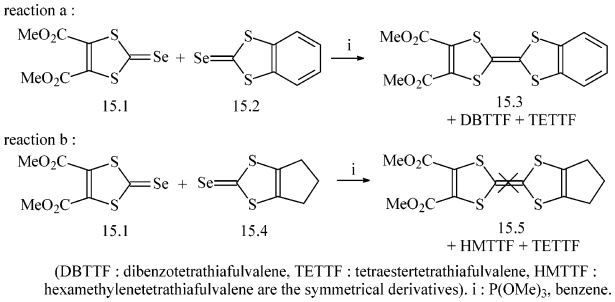
It was shown that, beside the crucial role played by the temperature, the concentration, and the nature of the phosphorus reagent in the success of the reaction, a thione substituted with electron withdrawing ester groups CO_2Me was most reactive with the triethyl phosphite reagent.[91]

The thiophilic attack of $P(OEt)_3$ on the C=S bond of **14.1**, led to the ylide intermediate *A* as an equilibrium mixture. The carbophilic attack of the carbanion of *A* on the C=S bond of the other thione (**14.2**) used in the reaction generated the adducts *B*,

Scheme 14

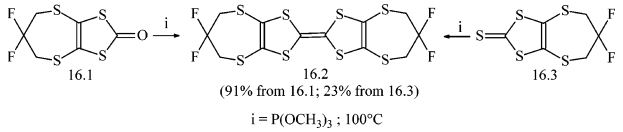


Scheme 15



(DBTTF : dibenzotetrathiafulvalene, TETTF : tetraestertetrathiafulvalene, HMTTF : hexamethylenetetrathiafulvalene are the symmetrical derivatives). i : $P(OMe)_3$, benzene.

Scheme 16



which then gives *C* by loss of $S{=}P(OEt)_3$. A new nucleophilic attack of *C* by $P(OEt)_3$ led to the intermediates *D* and *E*. Finally *E* gave the target TTF **14.3** by loss of a second $S{=}P(OEt)_3$ entity.

Disadvantages and Advantages. The principal advantage of this strategy is the facile access (generally three steps)[1] to a very large variety of 1,3-dichalcogenole-2-chalcogenones used as starting compounds in these reactions.[16,20] It presents also several disadvantages.

First of all, the success of the coupling reaction appears to depend strongly on the nature of the substituents on the 1,3-dichalcogenole-2-chalcogenones used. This was in particular observed (Scheme 15) in the condensation of the selenone **15.1** with the selenones **15.2** and **15.4**, respectively. When substituted by a benzo group, **15.2** led (reaction a)[92] to the expected TTF **15.3** accompanied by the corresponding symmetric species, whereas the replacement of the benzo group by a cyclopentyl group in **15.4** did not give (reaction b) the target dissymmetric TTF but only the two products of self-condensation: HMTTF (hexamethylenetetrathiafulvalene) and TETTF (tetraestertetrathiafulvalene).[93]

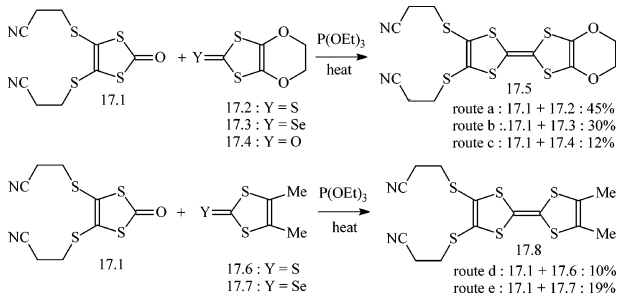
Another disadvantage of this strategy lies in the difficulty in the choice of the appropriate chalcogenone to be used to obtain the desired TTF. This question arises from the unpredictable difference in reactivity of the three types of chalcogenone (one, thione, and selenone) (also named oxone, thioxone, and selenoxone) in a trialkyl phosphite medium.

In the symmetric series it was indeed observed that the synthesis of BEDO-TTF (bisethylenedioxytetrathiafulvalene) was obtained in better yield (35%) through reaction with the 4,5-ethylenedioxo-1,3-dithiole-2-selenone rather than with the corresponding dithiole-thione (15%) or dithiole-one (5%).[94] Even more significant variations of reactivity were recently observed in the synthesis of the fluorinated symmetric TTF **16.2** (Scheme 16).[95]

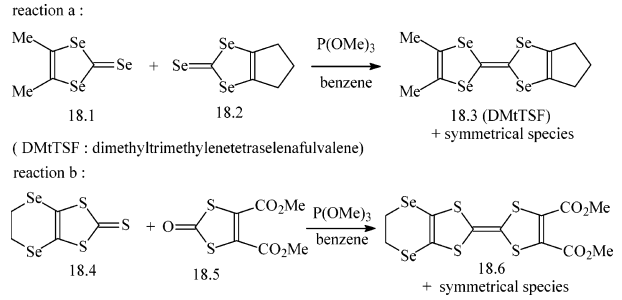
In contrast to the preceding example, the most reactive dithiole-one **16.1** led to 91% of TTF **16.2** whereas, under the same conditions, the corresponding dithiole-thione **16.3** gave only 23% of TTF **16.2**.

In the nonsymmetric series, the difficulty in the choice of the chalcogenone to be used is even greater

Scheme 17



Scheme 18



because there is no rule which allows prediction of which combination of chalcogenones (one/one, one/thione, one/selenone, etc.) will give the highest yield of the desired dissymmetric TTF. This difficulty is clearly illustrated (Scheme 17) by the synthesis of the protected bis(cyanoethylthio)TTF **17.5** and **17.8**,[96] the importance of which will be further seen below.

It is observed that the combination one/thione (**17.1/17.2**) which is most favorable to the preparation of TTF **17.5** (45%: route a) is also the least effective (**17.1/17.6**) in giving the derivative **17.8** (10%: route d). Despite often contradictory results, it was recently indicated that the yield in dissymmetric TTF can generally be significantly increased when a dithiole-one is coupled with a dithiole-thione.[97] This result is probably due to the more marked capacity of the dithiole-thiones to form ylide *A* (Scheme 14) and to the greater facility of the dithiole-ones to undergo nucleophilic attack on the carbon of the C=O bond.

Another disadvantage of this strategy is the formation of the two symmetric species besides the dissymmetric TTF.[1,16,98−108] Depending on the relative polarity of the three products obtained as a mixture, the separation of the target TTF can be particularly difficult, as in the case of DMtTSF **18.3** (dimethyltrimethylenetetraselenafulvalene) (Scheme 18a),[98] or, on the contrary, relatively easy, as for the functionalized TTF **18.6** (Scheme 18b)[108] and its sulfur derivative.[109]

This is why this strategy has been largely used to prepare functionalized TTF that can be easily separated from the formed mixtures.[20,96] Many functions have thus been introduced on TTF and TSF, in particular ester groups ($COOCH_3$)[1,16] which can be then easily converted into carboxylic acid (COOH), acid chloride (COCl), or amide ($CONH_2$)[110−114] or into the corresponding nonsubstituted derivative (H) by a simple decarboxymethylation.[80,110,111,115−118] Other functional groups incorporated include alcohol (OH),[119−124] phenol (ArOH),[125] aldehyde (CHO),[126,127]

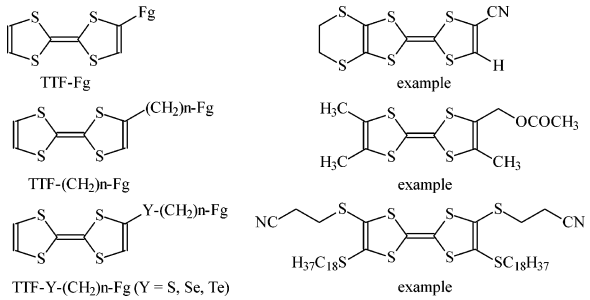
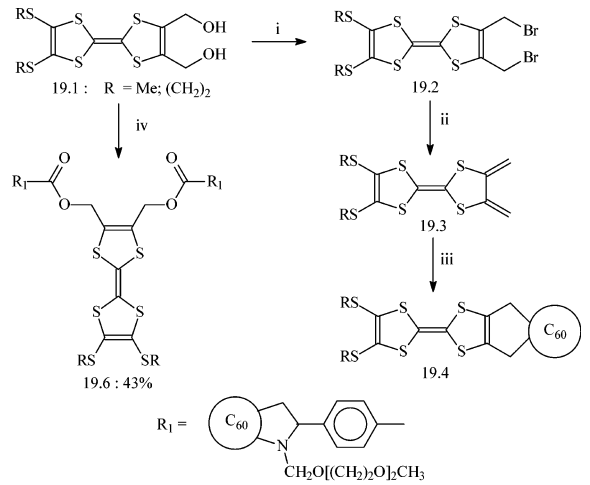


Figure 1.

Scheme 19



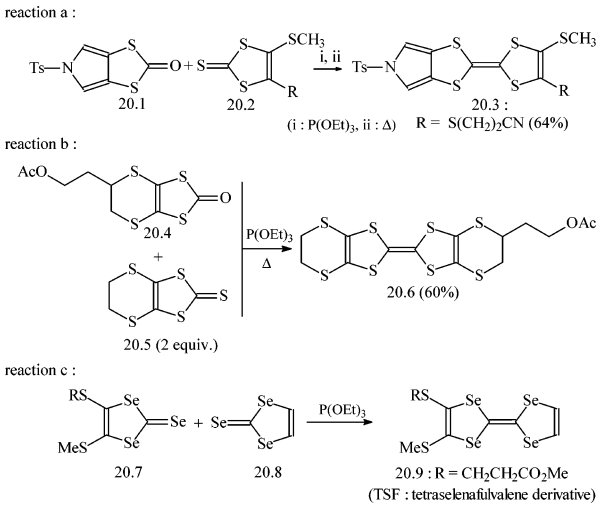
amide/lactam (CONH-),[128] nitrile (CN),[13,15,96,122,129,130] and halogen (X = Cl, Br, I).[124,131,132] These functional groups (Fg) can be linked either directly to the TTF ring [TTF−Fg] or by means of an alkylene chain [TTF−$(CH_2)_n$−Fg] or an alkylene chalcogeno spacer [TTF−Y−$(CH_2)_n$−Fg] (Y = S, Se, Te).[130−137] See Figure 1 for some examples.

Stable organic radicals were also introduced into the TTF skeleton using this route.[138] It is also interesting to note that, using the reduction of bis(carbomethoxy)-TTF[108,139,140] into the corresponding hydroxymethyl derivative then converted into the bis(bromomethyl)-TTF[140] by action of PBr_3, it was possible to link C_{60} to TTF[82,141] and to build photoactive systems and donor−acceptor molecular entities[82,141−145] (Scheme 19).

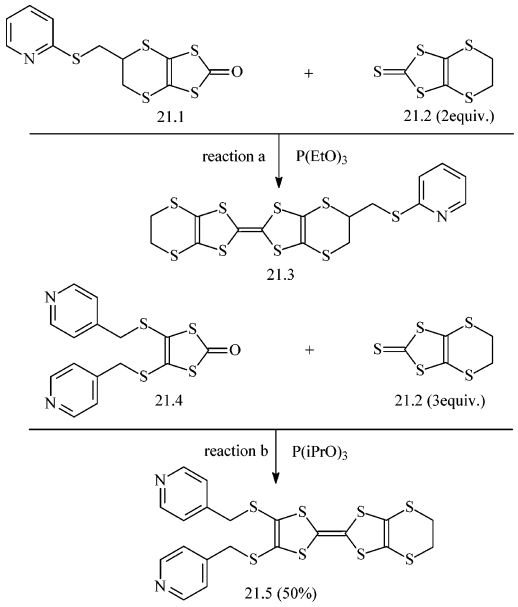
Recent Examples of the Use of Strategy IIb. Despite its disadvantages, this strategy is still very much used today, as shown by the large number of recent reports on the preparation of asymmetric TTF with very varied objectives.[49,84,133−137,146−153] The three following examples illustrate the very recent use of such a cross-coupling one/thione reaction.

The first shows the preparation of a functionalized TTF then used as a basic unit in the construction of a supramolecular system (Scheme 20).[49,132,135] The coupling one/thiones **20.1/20.2** and **20.4/20.5** in neat triethyl phosphite have respectively led (reactions a and b) to the expected functionalized TTFs **20.3** and **20.6** in variable yields after column chromatography purifications.[89,135] Under the same conditions, cross-coupling of the selenones **20.7/20.8** gave the dissym-

Scheme 20



Scheme 21



metric TSF (tetraselenafulvalene) **20.9** in 40% yield[154] (reaction c).

The second example concerns the synthesis of TTF linked to a porphyrin group[152] or to pyridine type ligands as potential precursors of salts combining coupled electrical and magnetic properties (Scheme 21).[135,137] The cross-coupling one/thione reactions in an alkyl phosphite medium (reactions a and b), with excess thione, led to the expected TTF in quite high yields after separation of the symmetric byproducts.

The third case is the synthesis of bis-fused TTF derivatives containing a tetrathiapentalene structure known to give conducting salts. Such derivatives were recently prepared (Scheme 22) by the use of strategy IIb,[146,148] although very low yields (10−20%) were obtained for derivative **22.3** and a whole series of related compounds.

It is also interesting to note that other symmetric and nonsymmetric TTFs (Figure 2) were very recently obtained, in particular by coupling reactions of dithiole-ones.[133,134,149,150]

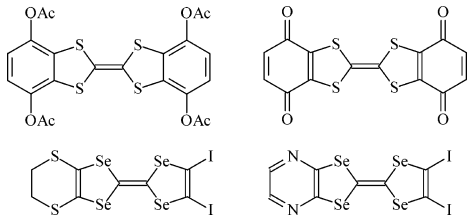
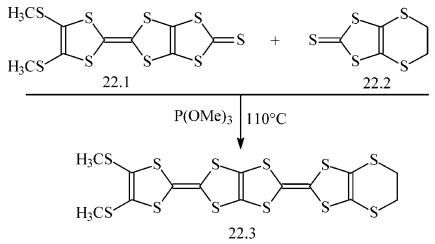


Figure 2.

Scheme 22



3.2. Selective Strategies: Condensation Reactions

To avoid the formation of the mixtures which characterize the preceding methods of synthesis, three new routes have been proposed to try to selectively obtain the dissymmetric TTF.

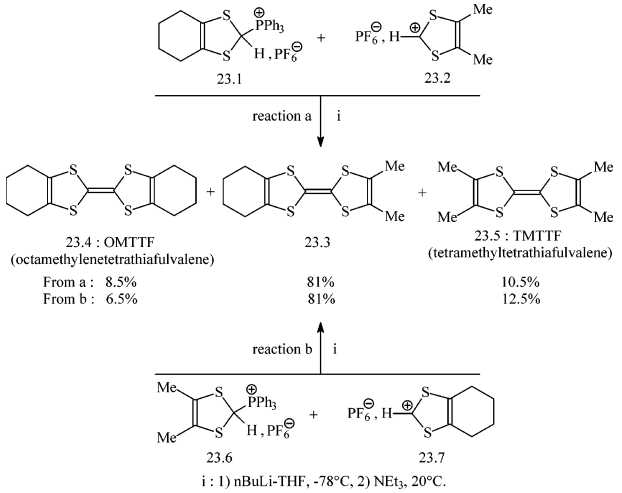
3.2.1. Strategy IIc: Partially Selective Wittig Type Condensation

Cava et al. were the first to describe a selective preparation of benzo-TTF derivatives based on a Wittig type condensation.[93] However, it was quickly observed that this reaction was not completely selective.[155−157] This was in particular shown with the synthesis of the dimethyl(tetramethylene)tetrathiafulvalene **23.3** (Scheme 23),[155] which was isolated as the main compound, besides a small amount of the two symmetric byproducts OMTTF (octamethylenetetrathiafulvalene) (**23.4**) and TMTTF (tetramethyltetrathiafulvalene) (**23.5**).

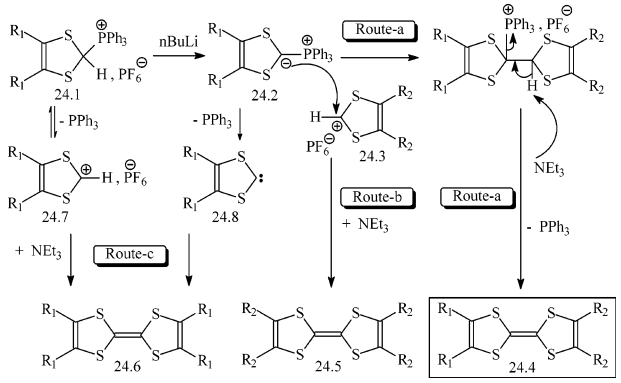
Mechanism. The formation of the three products of the mixture was explained by the mechanism described in Scheme 24.

Deprotonation of the phosphonium salt **24.1** by *n*BuLi into the ylide **24.2**, which reacts by nucleophilic addition to the dithiolium salt **24.3**, led to the

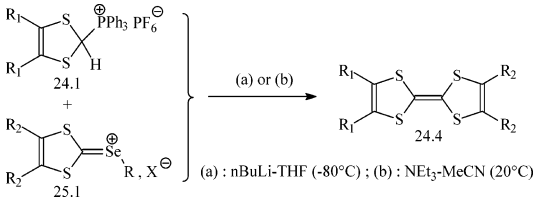
Scheme 23



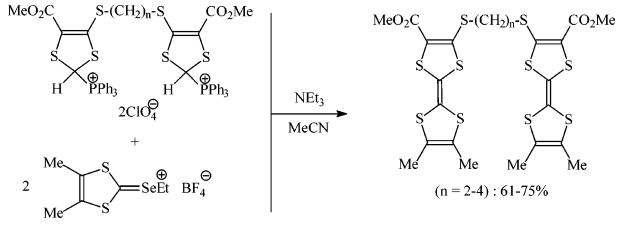
Scheme 24



Scheme 25



Scheme 26



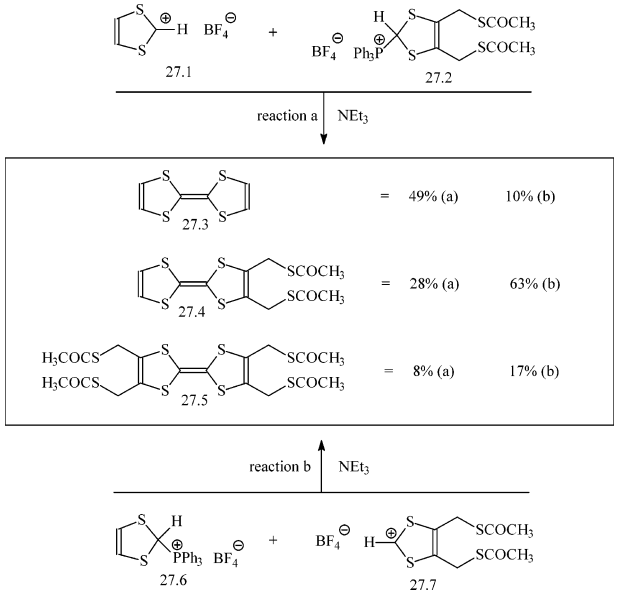
corresponding adduct. The latter undergoes deprotonation by Et_3N to give the expected nonsymmetric TTF **24.4** (route a), alongside PPh_3 as a byproduct. The formation of the symmetric compound **24.5** (route b) is probably due to the basic coupling reaction (Et_3N) of the dithiolium salt **24.3** via the corresponding carbene according to the mechanism of strategy IIa already seen in Scheme 9. The formation of the other symmetric compound **24.6** could be similarly explained (route c) if an equilibrium is assumed between the phosphonium and the dithiolium salts **24.1** and **24.7**, respectively. As suggested by Sudmale and co-workers,[158] the intrinsically unstable ylide **24.2** could decompose into the carbene **24.8**, which then undergoes dimerization (route c) to give the TTF **24.6**.

Disadvantages and Advantages. Undoubtedly, the main advantage of this strategy is the progress made in the selectivity of the reaction, which led to its use for the preparation of numerous dissymmetric TTF type molecules.[159−162] Moreover, further improvement was made by replacing the dithiolium salt **24.1** by a 2-chalcogenolium salt **25.1**, which is obtained more easily and avoids the formation of one of the two symmetric species (Scheme 25).

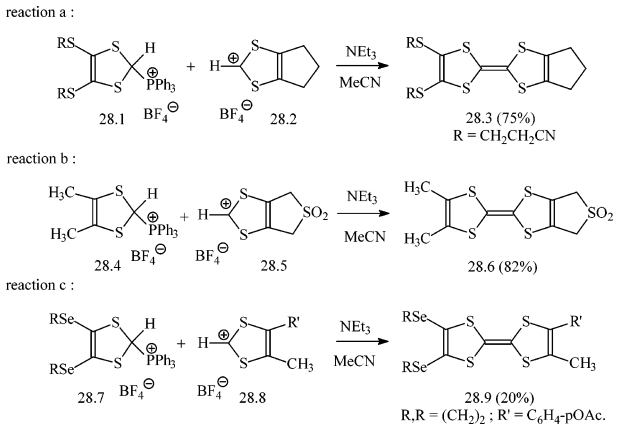
This improved method has also been very often used to prepare a large number of functionalized nonsymmetric TTFs,[161−165] in particular single bridged bis-TTF,[158] as illustrated in Scheme 26.

The main disadvantage of the strategy remains the formation of at least one of the two symmetric species

Scheme 27



Scheme 28



in addition to the target TTF. Moreover, it was recently shown[84] that, by using the coupling reaction between a phosphonium and a dithiolium salt, the selectivity of the reaction depends considerably on the nature of the substituents in the two salts used, as demonstrated by the synthesis of the TTF **27.4** (Scheme 27).

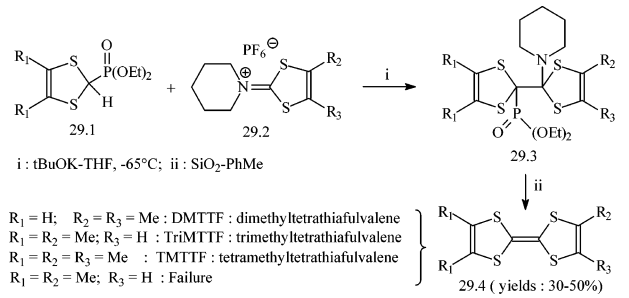
It is indeed observed that the undesirable symmetric TTF **27.3** is mainly obtained (49%) (reaction a), due to the self-coupling reaction of the salt **27.1** in the presence of Et_3N, whereas, by reversing the nature of the substituents (reaction b), the cross-coupling reaction between the dithiolium salt **27.7** and the ylide derived from the triphenylphosphonium salt **27.6** leads to the expected dissymmetric TTF **27.4** in 63% yield.

Recent Examples of the Use of Strategy IIc. Despite the above drawbacks, this strategy was still recently employed to prepare functionalized TTF precursors of both neutral molecular metals (Scheme 28a)[166,167] and conducting charge-transfer complexes (Scheme 28b,c).[148,168,169]

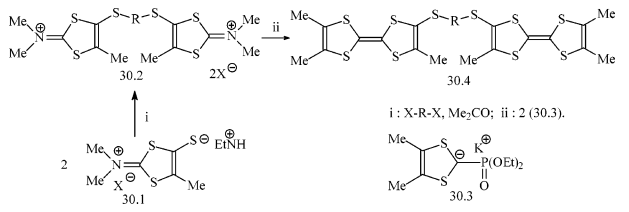
3.2.2. Strategy IId: Selective Horner−Wadsworth−Emmons Condensation

To suppress the formation of the self-coupling products observed in the Wittig type method, Ler-

Scheme 29



Scheme 30



strup and co-workers[170] applied (Scheme 29) Horner−Wadsworth−Emmons (or HWE) olefinations based on the reaction of a 1,3-dichalcogenole-2-phosphonate (**29.1**) with a 1,3-dichalcogenole-2-iminium salt (**29.2**) followed by an acidic deamination of the adduct intermediate formed (**29.3**).[170−172]

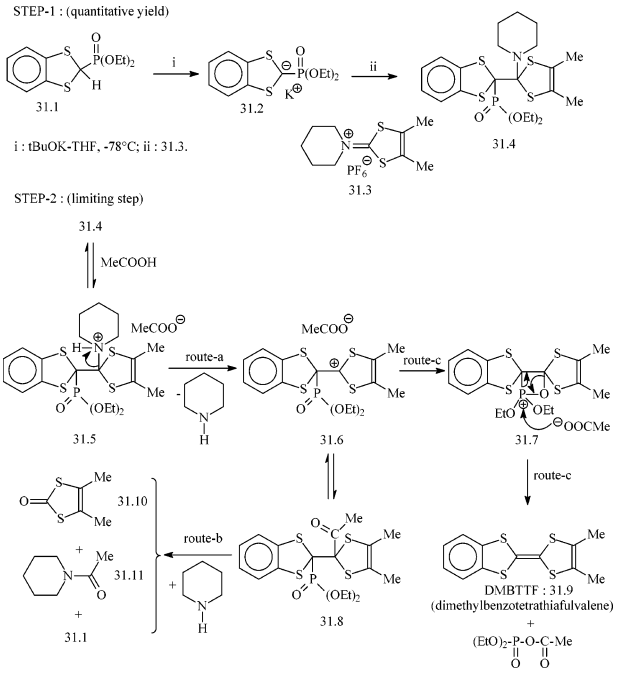
Disadvantages and Advantages. This entirely selective method has been employed in the synthesis of a great number of functionalized TTF derivatives[81,115−117] and of TTF partially substituted with selenium atoms.[173−175] As illustrated in Scheme 30, the double olefination was also used in the preparation of single bridged bis-TTFs[176,177] such as **30.4**.

Low yields were obtained in many cases,[174,178−180] and a study of the mechanism of the reaction was carried out using the synthesis of DMBTTF (dimethylbenzotetrathiafulvalene) as a model (Scheme 31).[181,182]

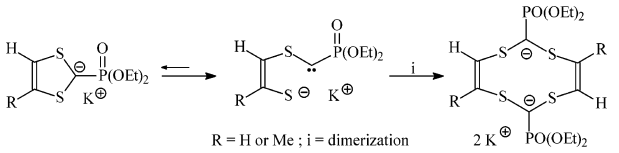
Mechanism. It was established that the first step of the mechanism quantitatively provides the adduct **31.4**. The nucleophilic addition of the phosphonate carbanion **31.2**, generated from benzo-1,3-dithiole-2-phosphonate **31.1** by proton abstraction, to the piperidinium salt **31.3** allows the quantitative formation of the adduct **31.4** which, however, is air-sensitive and decomposes to give **31.1** at 65 and 110 °C.

The second stage corresponds to the acidic deamination of the adduct **31.4**. This intermediate is initially protonated by anhydrous CH_3CO_2H to give to **31.5**, which undergoes deamination to afford the acetate intermediate **31.6** (route a) via piperidine elimination. At this stage the acetate **31.6** in equilibrium with **31.8** can evolve according to two possible directions: On one hand (route b), the intermediate **31.8** undergoes nucleophilic addition of the piperidine to the ester function to give the dithiole-one **31.10**, the acetylpiperidine **31.11**, and the phosphonate **31.1**. On the other hand (route c), the cyclization of **31.6** forms the oxaphosphetane-type intermediate **31.7**, which, via the nucleophilic addition of the acetate anion, collapses to produce the expected DMBTTF (dimethylbenzotetrathiafulvalene) and mixed anhydride $(EtO)_2PO(OAc)$.

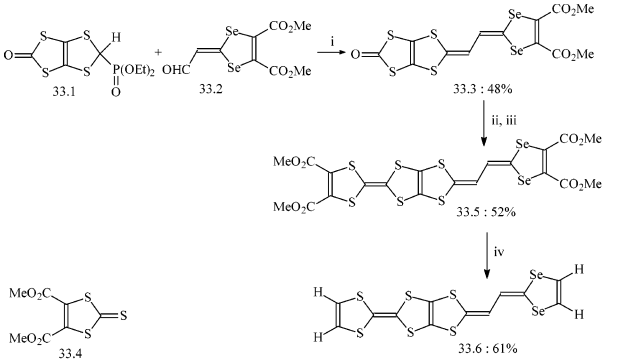
Scheme 31



Scheme 32



Scheme 33

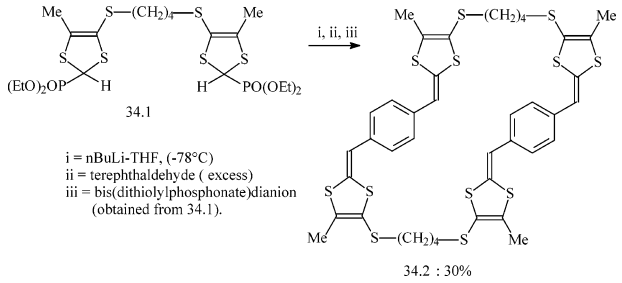


On the basis of these results, the development of a "one pot" procedure, without isolation of intermediate **31.4**, allowed a considerable enhancement of the yield of the products in the synthesis of unsymmetrically substituted TTF.[183] Nevertheless, low yields were observed when nonsubstituted 1,3-dithiole-2-phosphonates were used, because the corresponding phosphonate carbanions favor the ring-opened forms, which easily undergo dimerization (Scheme 32).[184]

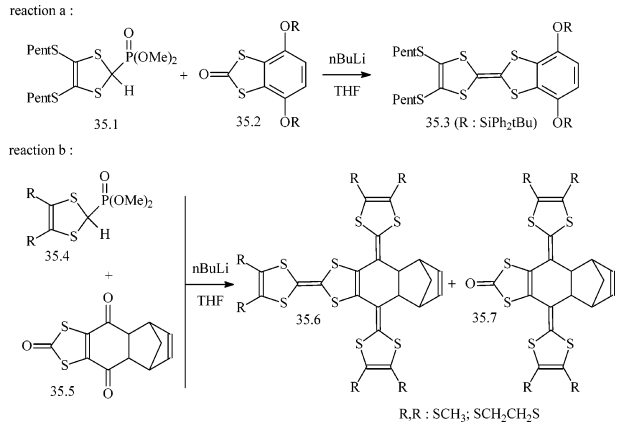
Recent Examples of the Use of Strategy IId. More recently the phosphonates necessary for this strategy IId were exploited in the synthesis of the selenium-containing bis-fused TTF vinylogues (Scheme 33).[185]

In addition (Scheme 34),[186,187] through successful twofold olefination by action on aromatic dialdehydes, these phosphonates allow formation of the macrocy-

Scheme 34



Scheme 35



clic compound **34.2**, incorporating two π-extended TTF units, in each of which the two dithiole rings are separated by a π-conjugated spacer.

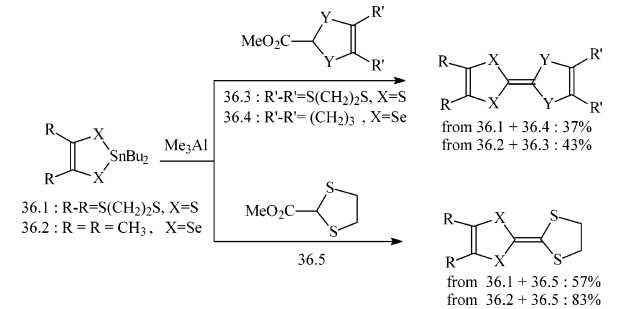
It is also interesting to note that recently the HWE olefination[188,189] was used to create TTF precursors for intramolecular electron-transfer systems[150] (Scheme 35a)[188] and to build rigid TTFs with an extended π conjugated structure, precursors of two-dimensional conducting solids[189,190] (Scheme 35b).

As shown by these examples, the olefination reaction occurs directly on the C=O double bond of the 1,3-dithiole-2-ones **35.2** and **35.5** and does not require the use of 1,3-dithiole-2-iminium salts generally preferred for their electrophilic character.

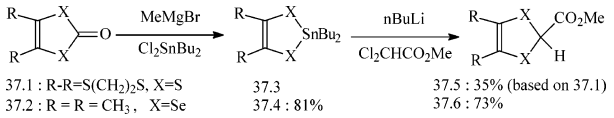
3.2.3. Strategy IIe: Organometallic Selective Yamada Condensation

A nonphosphite coupling synthesis of dissymmetric TTF was developed by Yamada et al. in 1995.[191−193] It is an entirely selective organometallic synthesis based on the reaction of an organotin dichalcogenolate with an ester in the presence of a Lewis acid such as $Al(Me)_3$, which appeared to be the most effective catalyst (Scheme 36).[191]

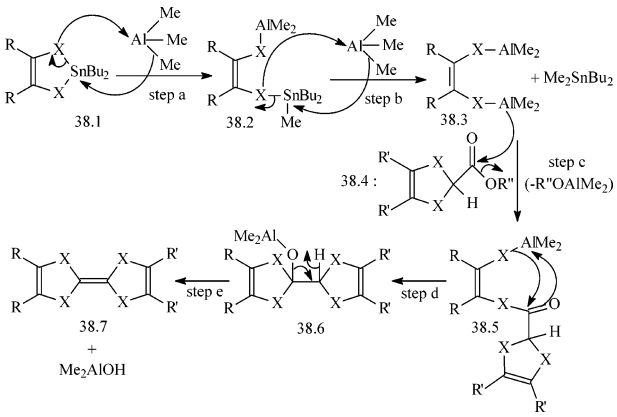
Scheme 36



Scheme 37



Scheme 38



The starting compounds are generally easily obtained from suitable chalcogenones (Scheme 37).[191]

Treatment of the dithiole-one (**37.1**; **37.2**) with MeMgBr in dry THF followed by trapping with dichlorodibutyltin (Cl_2SnBu_2) gives easily the organotin dichalcogenolate derivative (**37.3**; **37.4**).

For the desired ester part, the transmetalation of the organotin compound with 2 equiv of *n*BuLi, followed by reaction with methyl dichloroacetate, gives the expected ester (**37.5**; **37.6**).

The method applies both to the preparation of varied dissymmetric TTFs and to the synthesis of dihydro-TTF (Scheme 36) starting from esters derived from dithianes such as **36.5**. It can also be extended to the synthesis of selenium-containing analogues, although in this case the coupling reaction is slower.[192,193]

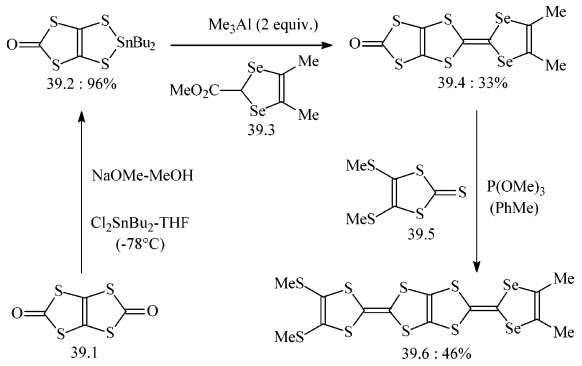
Mechanism. Although the mechanism of this Me_3-Al-promoted coupling reaction has not been studied in detail, it probably starts with a Sn/Al metal exchange reaction as shown in Scheme 38.

The tin−aluminum transmetalation (step a; b) of the organotin derivative **38.1** by Me_3Al leads to the bis(dimethylaluminum) dichalcogenolate **38.3**, which subsequently undergoes nucleophilic addition with the ester **38.4** to provide the chalcogenoester **38.5**. The intramolecular nucleophilic attack of the remaining aluminum chalcogenolate on the carbonyl function C=O followed by loss of Me_2AlOH produces the dissymmetric tetrachalcogenafulvalene **38.7**.

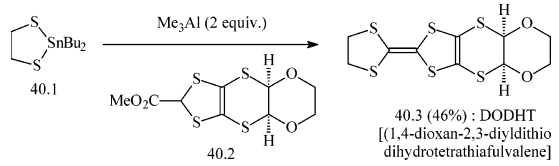
Besides the synthesis of numerous nonsymmetric TTFs, this method has also been extended successfully to the synthesis of original donors containing the tetrathiapentalene (TTP) unit and to the preparation of new fused bis-TTFs (Scheme 39) that lead to a series of materials exhibiting very high electrical conductivity.[194,195]

The thiapendione (**39.1**), generally used as starting compound, provides the partially selenium-containing derivative **39.4** via an organometallic coupling reaction. This is then converted into the fused-TTF **39.6** by the one/thione (**39.4**/**39.5**) cross-coupling

Scheme 39



Scheme 40



reaction carried out in the presence of trimethyl phosphite.

Disadvantages and Advantages. Although some rare failures have been noted in the synthesis of bis fused-TTF[191] by combination of this organometallic route and chalcogenone coupling (see Scheme 39), the approach generally gives quite high yields. In addition, it presents the advantage of having numerous applications, in particular for the preparation of a large number of TTFs, bis-fused TTFs,[196−199] and other types of organic donors.[200,201]

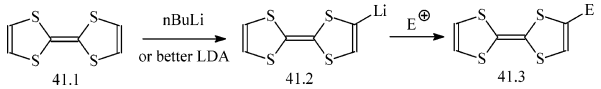
Recent Examples of the Use of Strategy IIe. This synthetic method is still widely used to prepare organic precursors for metallic materials and superconductors,[200,202,203] as exemplified in Scheme 40 by the synthesis of the organic donor DODHT (1,4-dioxan-2,3-diyldithiodihydrotetrathiafulvalene),[204] which contains both a reduced π-system and a nonplanar molecular structure and which has led to several new superconducting salts.[203−205]

4. Strategy III: Electrophilic Substitution of Metalated Tetrachalcogenafulvalenes

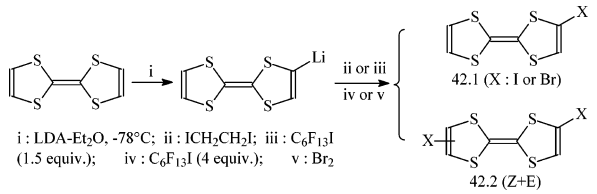
This strategy was proposed for the first time by Green,[206] who obtained a whole series of substituted compounds containing key functional groups,[206,207] starting from TTF.

Mechanism. The mechanism is related to the acidic character of the hydrogen atoms of TTF which can be substituted by lithium in a metalation reaction with *n*BuLi or LDA in particular. The air-sensitive tetrathiafulvalenyllithium obtained is highly reactive even at low temperature, and it reacts immediately with various electrophiles to give the corresponding functionalized or alkylated TTF by nucleophilic substitution (Scheme 41).

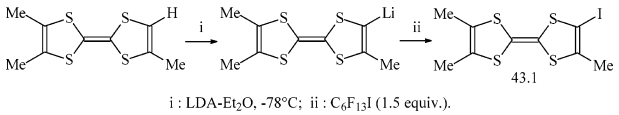
Scheme 41



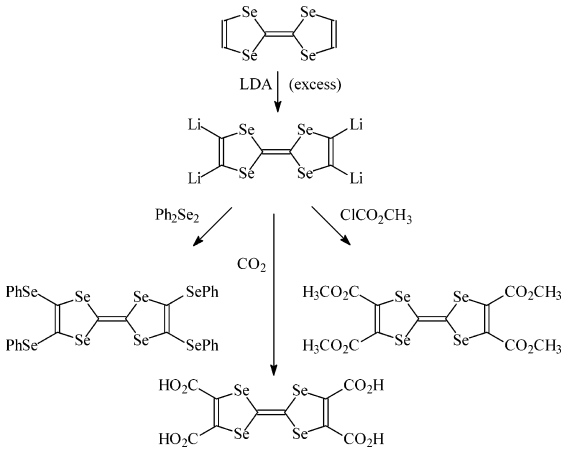
Scheme 42



Scheme 43



Scheme 44



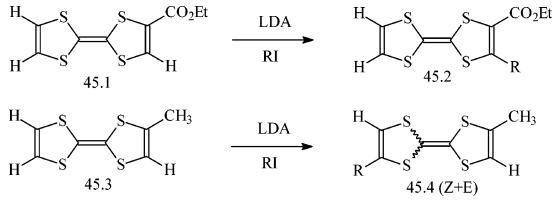
Disadvantages and Advantages. The first disadvantage of this strategy is the need to first prepare TTF in six steps[172,208] (although this expensive compound is now available from Aldrich) or prepare TSF, which is still tedious[209−212] despite the new method very recently proposed for alkylenedithio-TSF[154] in particular.

Moreover, as first mentioned by Green[206] and again by Garin[213] in an excellent review article on this type of reaction, the main disadvantage of this strategy is the disproportionation of tetrathiafulvalenyllithium into multilithiated species, which occurs even at −80 °C and often results in a complex mixture of products along with the recovery of TTF, as shown in the synthesis of halogenated TTF[214−217] (Scheme 42).

However, for functionalized TTFs of different polarities, the separation of the components of the mixture is in general easy, unlike the case of alkylated TTFs, for which the polarities are very close. Of course, this problem disappears when a trialkylated TTF (or TSF) is used as a starting material,[178,218−220] as, for example, in the synthesis of iodotrimethyl-TTF (Scheme 43),[178,218] or when the TSF is converted into the tetralithiated derivative by 4 equiv of LDA to lead to the tetrasubstituted TSF in the presence of an excess of electrophilic reagent (Scheme 44).[221−224]

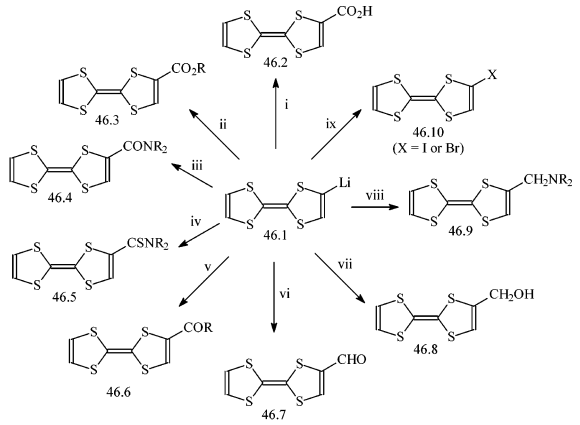
In the case of monosubstituted TTF (Scheme 45), the orientation of the lithiation depends on the nature of the substituent already present on the TTF heterocycle. An electron withdrawing substituent such as CO_2Et increases the acidity of the adjacent

Scheme 45



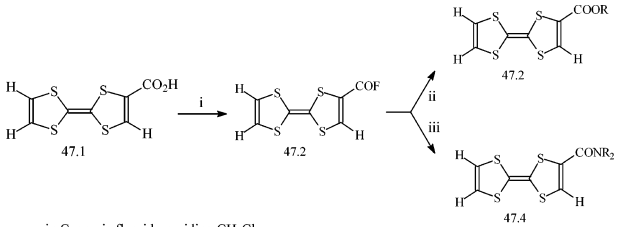
45.1 45.2 45.3 45.4 (Z+E)

Scheme 46



i : CO_2, -78°C -> 20°C; HCl/H_2O, 20°C. ii : $ClCO_2R$ -78°C -> 20°C; H_2O. iii : PhN=C=O,-78°C -> 20°C; H_2O. iv : PhN=C=S,-78°C -> 20°C; H_2O. v : MeCOCl or PhCOCl, -78°C -> 20°C. vi : Ph(Me)NCHO or DMF, -78°C-> 20°C; HCl/H_2O. vii : HCHO, -78°C -> 20°C; H_2O. viii : $CH_2=NR_2$ I, -78°C -> 20°C; H_2O. ix: PFHI or NBS, -78°C -> 20°C; H_2O.

Scheme 47



i : Cyanuric fluoride-pyridine-CH_2Cl_2.
ii : ROH-DMAP (ROH : EtOH = 99% yield, BuOH =97%, PhOH = 95%, $Me(CH_2)_{15}OH$ = 93%)
iii : R_1R_2NH (R_1R_2NH : $Me(CH_2)_{17}NH_2$ = 99%, Me_2NH = 98%, $PhNH_2$: 97%).

hydrogen atom and leads to a 4,5-disubstituted TTF (**45.2**) after alkylation whereas an electron donor substituent (CH_3), which decreases this acidity, directs the lithiation to the unsubstituted 1,3-dithiole ring (**45.3)** that then gives the two diastereoisomers Z/E[207,213] of the disubstituted TTF **45.4**.

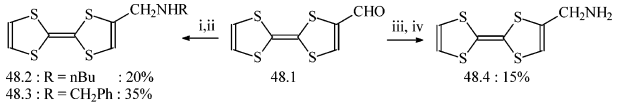
Despite these disadvantages, the method has several significant advantages. It allows the preparation (Scheme 46) of a large variety of donors carrying the major organic functions[178,206,207,219] by direct functionalization of the TTF or TSF skeleton.

Depending on the final objective, these functions can then be converted into others[213] to give new precursors for conducting materials or, in certain cases, can be used to prepare varied bis- and tris-TTF. Some typical examples of such transformations are described below.

Transformation of TTF−CO_2H into TTF−CO_2R and TTF−$CONR_2$. A first example of the transformation of a function is given (Scheme 47) with the conversion of a carboxylic acid into an ester or amide via[225−227] the corresponding acid chloride[110] or, more efficiently, via the acid fluoride.[228]

Transformation of TTF−CHO into TTF−CH_2NR_2. Another interesting transformation is the

Scheme 48

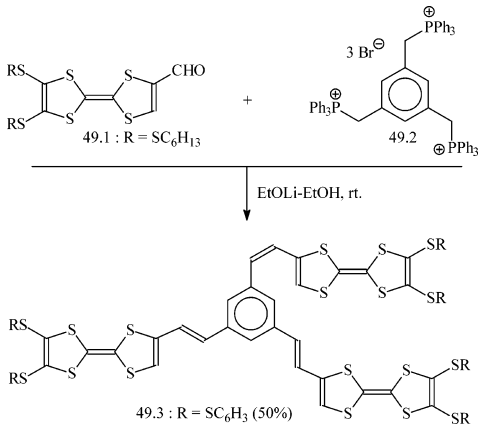


48.2 : R = nBu : 20%
48.3 : R = CH_2Ph : 35%

48.1 48.4 : 15%

i : RNH_2-CH_2Cl_2, Al_2O_3,. ii : $LiAlH_4$-Et_2O; iii : $\overset{\oplus}{H}ONH_3,\overset{\ominus}{Cl}$-pyridine-EtOH; iv : $LiAlH_4$-Et_2O

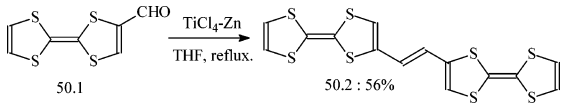
Scheme 49



49.1 : R = SC_6H_{13} 49.2

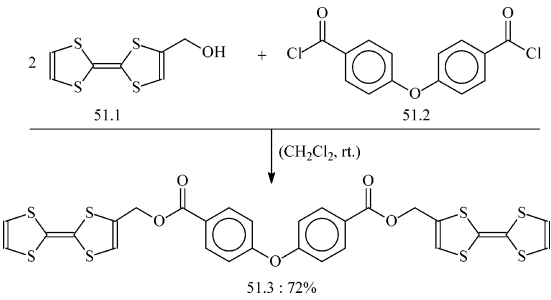
49.3 : R = SC_6H_3 (50%)

Scheme 50



50.1 50.2 : 56%

Scheme 51



51.1 51.2 51.3 : 72%

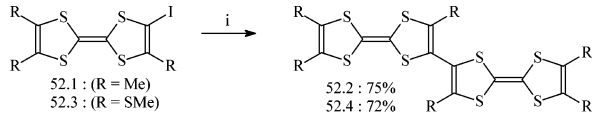
conversion of formyl TTF (TTF−CHO) into amino-TTF (Scheme 48)[229−231] because primary or secondary amines are able to lead to bidimensional conducting materials by creation of intermolecular hydrogen bonds in the solid state,[22] as in the case of amides[232]

The aldehyde function can also be used to lead to highly conjugated bis- and tris-TTF,[232−236] in particular. As shown in Scheme 49, TTF−CHO **49.1** engaged in a threefold Wittig type condensation with the tris-(triphenylphosphonium) salt **49.2**, to form the derivative tris-TTF **49.3**[233,234] with a yield of about 50%.[236]

In an alternative route (Scheme 50) a reductive coupling of TTF−CHO by a low-valent titanium reagent produced the bis-TTF derivative **50.2** with an ethene linker in a 56% yield.[235]

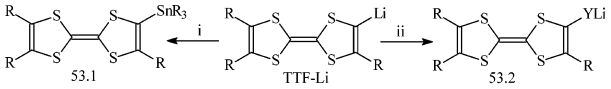
The aldehyde function is also easily reduced into alcohol,[126,213,237,238] which then allows the condensation of the obtained hydroxymethyl-TTF derivative with acid dichlorides to prepare intramolecular donor−acceptor systems[239] and oligo- and bis-TTF linked by a functionalized spacer. This is illustrated (Scheme 51) by the formation of the bis-TTF linked by ester-containing spacer groups usable as a stopperless axle suitable for pseudorotaxane molecular shuttles.[240]

Scheme 52



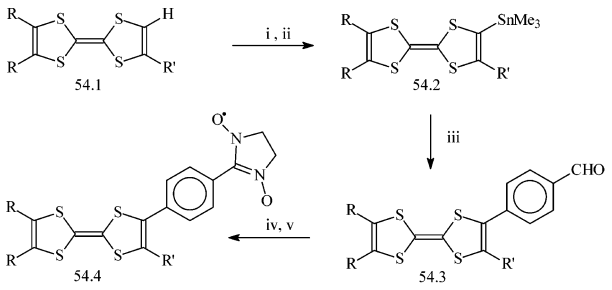
i : $Cu^{(I)}$-thiophene-2-carboxylate, (NMP, 20°C).

Scheme 53



i : Me_3SnCl or nBu_3SnCl, -78°C -> 20°C; ii: Y = S_8 or Se, -78°C -> 20°C. R = H, alkyl, S-alkyl..

Scheme 54



i : LDA-THF, -70°C; ii : Me_3SnCl-THF, -70°C; iii : XC_6H_4CHO (X=Br or I), $Pd(PPh_3)_2Cl_2$ PhMe, reflux ; iv : $[C(CH_3)_2(NHOH)]_2$, cat. $[C(CH_3)_2(NHOH)]_2.HSO_4^-$, CH_2Cl_2-Hexane (2:1) reflux ; v : PbO_2, K_2CO_3-THF, -20°C, a : R=R'=H, b : R-R'= SCH_2CH_2S, R'=H, c : R-R'= SCH_2CH_2S, R'= SMe. 53.3 : a = 50%, b : 60%, c : 55% yield.

The halogen function was also used to prepare bis-TTFs. In this case two TTF units are directly connected. Condensation results from the homo-coupling of iodo-TTF by treatment with copper in refluxing DMF (Ullmann coupling) or with copper(I) in *N*-methylpyrrolidinone (NMP),[63,178,217,218,241] as illustrated in Scheme 52.

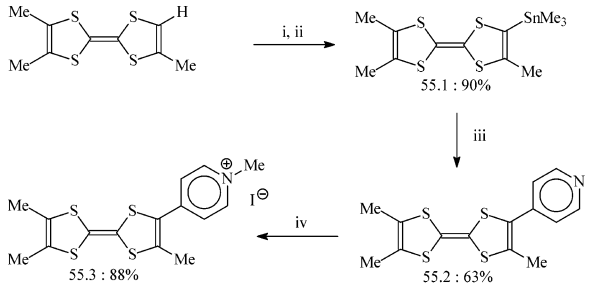
Another significant advantage of this strategy is the possible conversion of the tetrathiafulvalenyllithium (TTF−Li) into other key organometallic derivatives such as the corresponding stannyl and chalcogenolithiated derivatives **53.1** and **53.2** obtained at low temperature by action of trialkyl tin halide ($XSnR_3$)[242−247] or by insertion of sulfur, selenium, or tellurium in the C−Li bond[172,178,213,221] (Scheme 53), respectively.

Numerous new structures derived from TTF were prepared from these organometallic precursors, as shown through the series of examples presented below.

Use of Trialkylstannyl-TTFs: Stille Reaction. *Introduction of Specific Groups: Organic Radicals, and Aromatic Heterocycles.* The cross-coupling reaction of stannyl-TTF derivatives with aromatic halides in the presence of palladium catalysts allowed the direct or indirect introduction of specific groups into the TTF core. Recently, to try to construct ferro- and ferrimagnets, stable organic radicals were introduced into TTF by palladium catalyzed multistep cross-coupling of 4-halogenobenzaldehyde with trimethylstannyl-TTF (Scheme 54).[245]

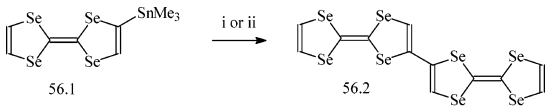
Similarly, to obtain donor−acceptor systems exhibiting intermolecular charge transfer, the Pd-catalyzed coupling of TTF with aromatic nitrogen heterocycles[247,248] was carried out, as shown (Scheme 55) by the reaction between a trialkylstannyl-TTF

Scheme 55



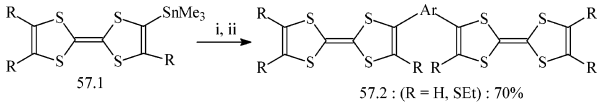
i : LDA-THF, -78°C; ii : Bu_3SnCl, -78°C -> 20°C; iii : 4-bromopyridine hydrochloride, $NaHCO_3$, PhMe, $Pd(Ph_3)_4$, reflux; iv : MeI-acetone, reflux.

Scheme 56



i : $Pd(OAc)_2$ (0.5 equiv.)-THF; ii : $Cu(NO_3)_2.3H_2O$ (0.5 equiv.)-THF.

Scheme 57



i : X-Ar-X; ii : $Pd(PPh_3)_4$-PhMe, reflux.

and 4-bromopyridine hydrochloride to prepare the *N*-methylpyridinium-substituted TTF derivative **55.3**[247] after subsequent alkylation by ICH_3.

It is also interesting to note that these organometallic condensations gave access to more complex structures containing several units of TTF or TSF.[46−49,246,249]

Introduction of Another TTF Unit: Bis-TTF Synthesis. Two tetrachalcogenofulvalene units can be directly connected as in the case of the bis-TSF obtained by the Pd- or Cu-mediated homo-coupling of TSF−$SnMe_3$ (Scheme 56).[249]

Conjugated bis-TTFs with aryl linkers, such as benzene, thiophene, pyridine, and azulene (Scheme 57),[243] have also been prepared from TTF−SnR_3 using this strategy.

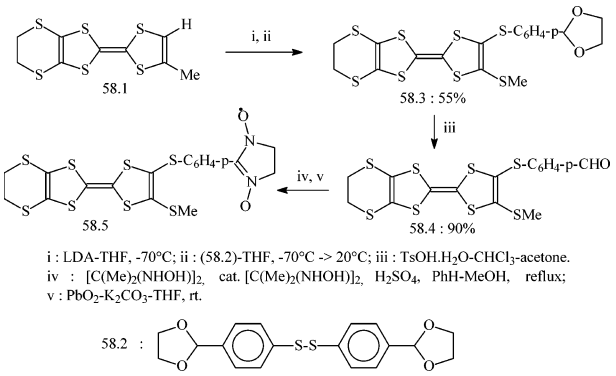
Use of Chalcogenolithiated-TTFs. Chalcogenolithiated TTF derivatives can be obtained by adding elemental sulfur or selenium to lithiated TTFs at a low temperature.[172,178,221,250]

The resulting compounds react easily with various electrophiles to lead, in particular, to chacogeno-TTFs substituted by specific groups, such as organic radicals,[245,251] as outlined by Scheme 58.[245]

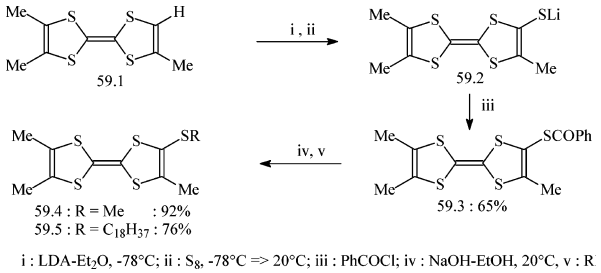
They can also lead to functionalized TTF of the TTF−Y−Fg type (with Y = S). The benzoyl functional group (Fg) can generally be used as a chalcogenolate protecting group which can then be deprotected in the presence of a base and finally alkylated (Scheme 59).[172,178]

The wide use of cesium and sodium chalcogenolate TTF salts must also be mentioned. These salts are easily obtained by basic deprotection (NaOEt in EtOH; $CsOH·H_2O$ in DMF) of mono- and bis(cyanoethylchalcogeno)-TTF accessible by almost all the strategies described above (see in particular Schemes 13c, 17, and 28a). This deprotection/alkylation method

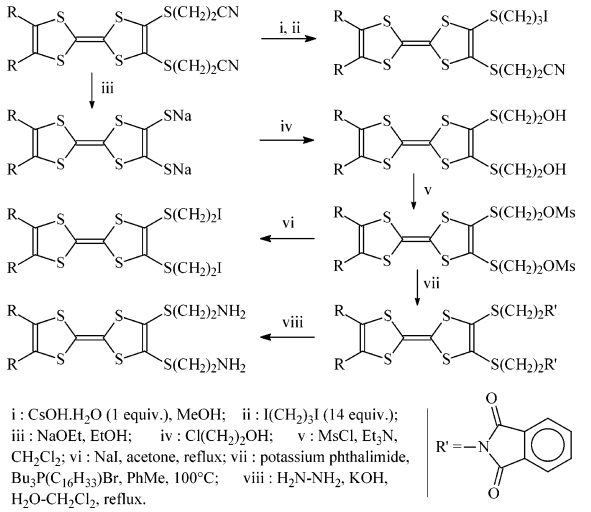
Scheme 58



Scheme 59



Scheme 60

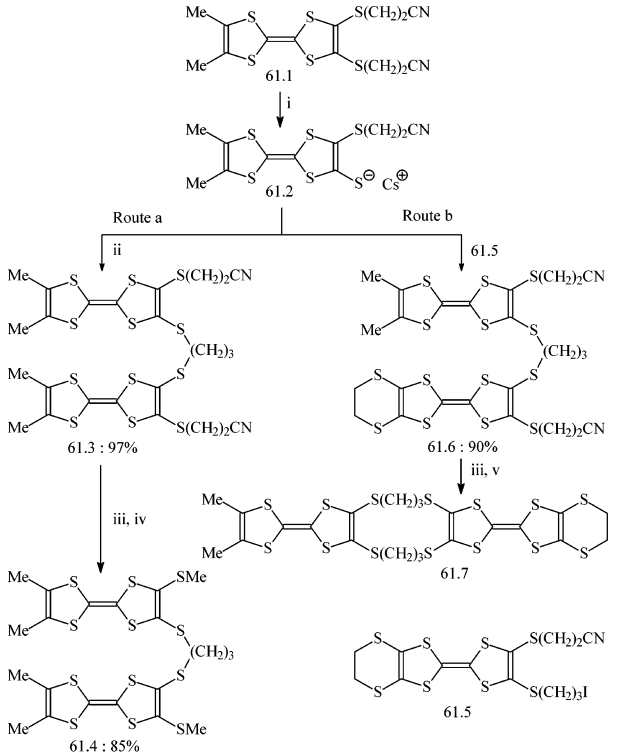


developed by Becher and colleagues[43,44,46,48,60,96,165,252,253] has made possible the introduction of various functional chains containing hydroxy,[13,15,96,164,254−256] halogeno,[55,122,257−259] amino,[115,117,122,256,260] and phosphino groups[250] into the TTF, as illustrated in Scheme 60.

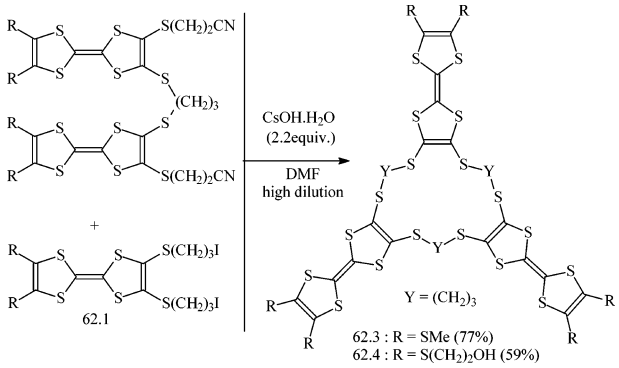
This method is also used for the preparation of numerous oligo-TTFs[55,60,67,252,255,258,262,263] and of a large variety of single and double bridged bis-TTFs (Scheme 61).[46−48,153,252,258]

The synthesis of bis-TTF is generally carried out in situ under basic conditions from mono-deprotection of the corresponding bis(cyanoethylthio)-protected TTFs by addition of cesium hydroxide (1 equiv) and subsequent reaction of the resulting mono-deprotected derivative with a diiodo derivative (0.5 equiv) under high dilution. It was also demonstrated that high dilution was not always necessary for the success of the twofold alkylation.[62]

Scheme 61



Scheme 62



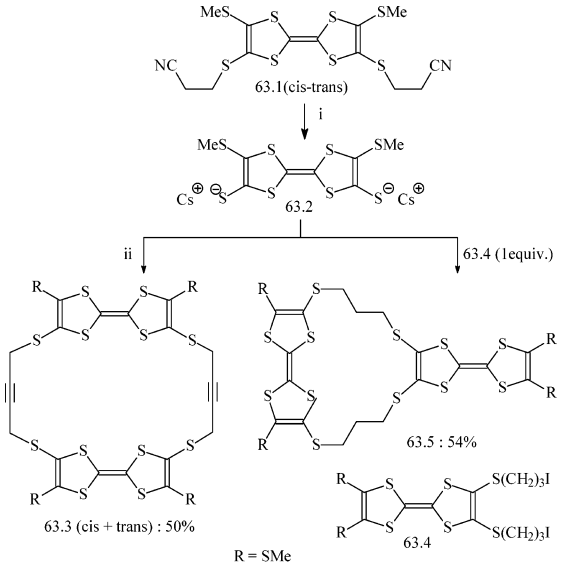
Furthermore, the bis TTFs can lead (Scheme 61) not only to the corresponding double-bridged bis-TTFs such as **61.7** by a twofold deprotection (CsOH·H_2O, 2.2 equiv) but also, depending on the reaction conditions and the nature of the diiodo compound used (Scheme 62), to a double-bridged bis-TTF macrocycle and to macrocycles comprising three, four, and even five TTF units.[252,262]

Additionally, depending upon the nature and the length of the diiodo spacer, the double deprotections of bis(cyanoethylthio)-TTFs under similar conditions have led to bis-TTF macrocycles exhibiting different geometries (Scheme 63).[67,252,253]

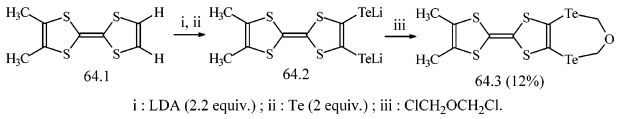
This method was also recently used in a multistep procedure to synthesize supramolecular architectures for the construction of molecular electronic systems[49] and to prepare TTF cyclophanes used as cage molecules able to incorporate organic molecules from solution inside the molecular cavity.[264]

Recent Examples of the Use of Strategy III. This strategy is still regularly used, as is shown by

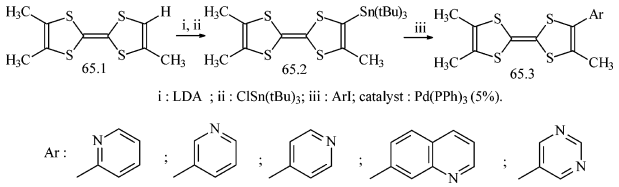
Scheme 63



Scheme 64



Scheme 65



the synthesis of dimethyl-TTF substituted by a tellurium-containing heterocycle (Scheme 64)[265] used as a precursor for conducting salts.

It is also important to mention the recent preparation, via this method (Scheme 65),[248] of TTFs substituted by nitrogen-containing aromatic ligands able to complex various paramagnetic transition metals, that are potential precursors for magnetic-conducting materials.

5. Conclusion

It has been shown through the different examples presented above that the preparation of dissymmetric TTFs, precursors to a multitude of materials and supramolecular structures, is a difficult task requiring the use of several synthesis strategies that have developed over the years. While the least efficient strategies are now abandoned, others have undergone successive modifications with the aim of increasing (with more or less success) the selectivity and yield of desired dissymmetric TTFs. Despite these efforts, it appears today that the selective methods, although essential, are not necessarily more used than the others.

Strategy I, based on the condensation of 1,2-dichalcogenolates with tetrachloroethylene (Schemes 3−5), is the oldest (1926) and is no longer used. It is

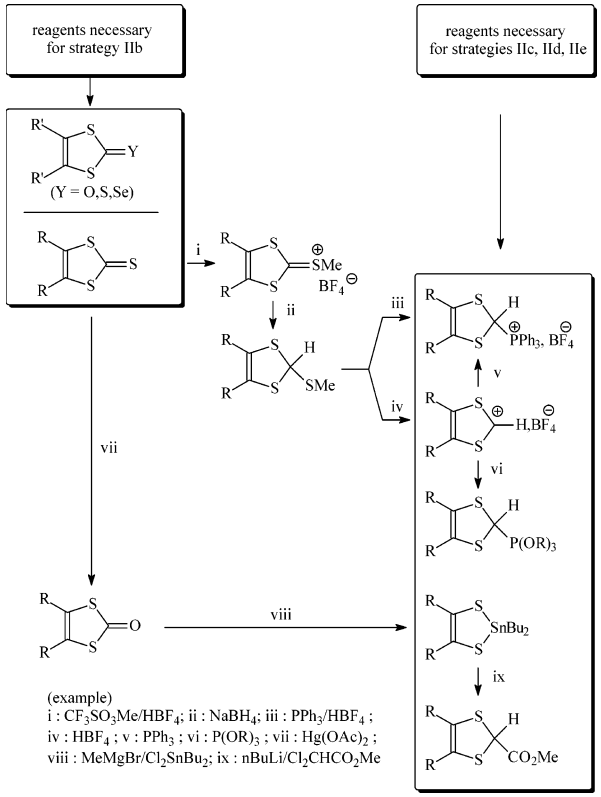


Figure 3.

nonselective, offers only poor yields, often leads to failure (Scheme 4), but gives access to tetratellurafulvalenes (Scheme 5).

Strategy II, particularly rich, incorporates several more or less selective methods (IIa−IIe) which correspond to the condensation of two 1,3-dichalcogenole rings (Scheme 6). The two first, IIa and IIb, based on cross-coupling reactions, are nonselective (Scheme 8) and have the disadvantage of forming mixtures of symmetrical and dissymmetrical TTFs that are often difficult to separate (Schemes 10, 11, and 13: IIa. Scheme 15: IIb). They remain however particularly interesting for the preparation of functionalized series because, in this case, the separation of the dissymmetric TTF from the formed mixture is largely facilitated by the difference in polarity of the isolated species (Schemes 17−22).

The three other strategies IIc, IId, and IIe, Wittig (Schemes 23, 25, and 28), Horner−Wadsworth−Emmons (Schemes 29, 30, and 33−35), and organometallic types, respectively (Schemes 36, 37, 39, and 40), were proposed successively to circumvent this disadvantage, and they are partially (IIc) and totally selective (IId, IIe). Despite this remarkable result, it is curious to note that for the synthesis of dissymmetric TTFs the nonselective approach IIb (Scheme 8) is used as much today, despite its disadvantages, as the selective strategies IIc, IId, and IIe (Schemes 23, 29, and 36).

This surprising observation is probably due to the fact that method IIb offers direct access to dissymmetrical TTFs from chalcogenone couplings, which avoids the multistep preparation of salts necessary for the selective strategies IIc, IId, and IIe (Figure 3).

Strategy III, based on the metalation of TTFs (Scheme 40), is dependent on the preceding routes, since, except for TTF and TSF, it uses an incompletely substituted dissymmetric TTF as starting compound (Schemes 43, 53−55, and 57−59). It is today under full development and is very largely used. It gives access in particular to a considerable variety of substituted dissymmetric TTFs (Schemes 54−59) via its key lithiated, stannylated, and chalcogenolithiated derivatives (Scheme 53). It is also a significant source of functionalized dissymmetrical TTFs (Schemes 44−46) that enable chemistry to be carried out at the periphery of the TTF, such as the functional modifications (Schemes 47−48) and the introduction of specific groups leading, for example, to various bis- and oligo-TTFs (Schemes 50−52).

In the continuity of this strategy the deprotection/alkylation method of chalcogenolates (Scheme 61) developed by Becher et al. from cyanoethylchalcogeno TTFs (Schemes 13c, 17: strategy II) is today one of the most used methods to obtain not only many functionalized dissymmetric TTFs (Scheme 60) but also a very large variety of oligo-TTFs and single- and double-bridged macrocyclic bis-TTFs (Schemes 61−63).

Finally, the growing current interest in organic materials and in supramolecular structures based on dissymmetric TTF molecules consolidates and confirms the importance of the still very largely used strategies outlined above.

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