

Figure 3.

diastereoselective and *m*-substituted benzyloxy carbene complexes were not selective at all.

In summary, we have described an unusual rearrangement reaction of arylmethoxy aryl carbene complexes of tungsten and chromium, which was observed as a

fortunate accident. But this also reminds us of the complexity of diverse reactivity patterns such organometallic compounds display, in order to challenge the wits of practising chemists.

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## Synthesis and properties of novel $\pi$ -electron donors—Variants of tetrathiafulvalene\*<sup>†</sup>

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*The remarkable one-dimensional conductivity exhibited by the charge transfer complex formed from tetrathiafulvalene (TTF) and tetracyanoquinodimethane has sparked attempts to synthesize related organic metals. In particular, the possibility of utilizing alternative  $\pi$ -donors has attracted considerable attention. In this article, the synthesis and electrochemical characterization of a number of TTF analogues with different olefinic and heterocyclic spacer groups are described.*

ORGANIC synthesis continues to play an increasingly important role in modern technology as we approach the twenty-first century. Almost everyone is familiar with liquid crystal displays in electronic equipment, watches and novelty devices. It is anticipated that organic

synthesis will lead to synthetic materials with metallic properties, conductors, superconductors, ferromagnets, NLO materials, photoconductors, etc. Synthetic metals are bound to find applications in electronics, plastic batteries etc. Photoconductors, semiconductors and superconductors have applications in photocopiers, solar cells, computer logic gates, etc.<sup>1</sup>.

The focus of this article is limited to the synthesis and properties of compounds which may be important in the design of organic conductors or superconductors.

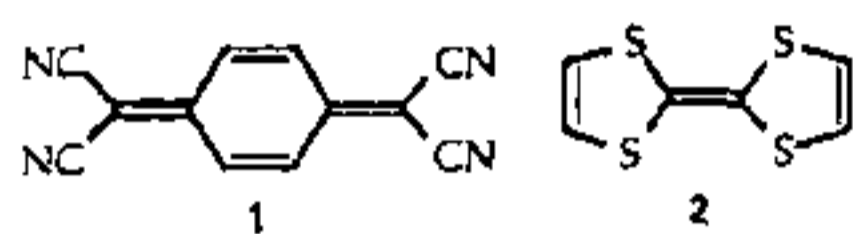
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\*Dedicated to Prof. T. R. Govindachari on his 77th birthday.

<sup>†</sup>Based on a talk given at the Third NOST Symposium held at Bhubaneswar in December 1992.

About two decades ago virtually no conducting organic materials were known. They were insulators [ $\sigma$  between  $10^{-20}$  to  $10^{-6}$  ( $\text{ohm/cm})^{-1}$ ]. The semiconductors like germanium and silicon have  $\sigma \sim 10^{-2}$  ( $\text{ohm/cm})^{-1}$  followed by the metals whose  $\sigma$  varied from 1 to over  $10^8$  ( $\text{ohm/cm})^{-1}$ .

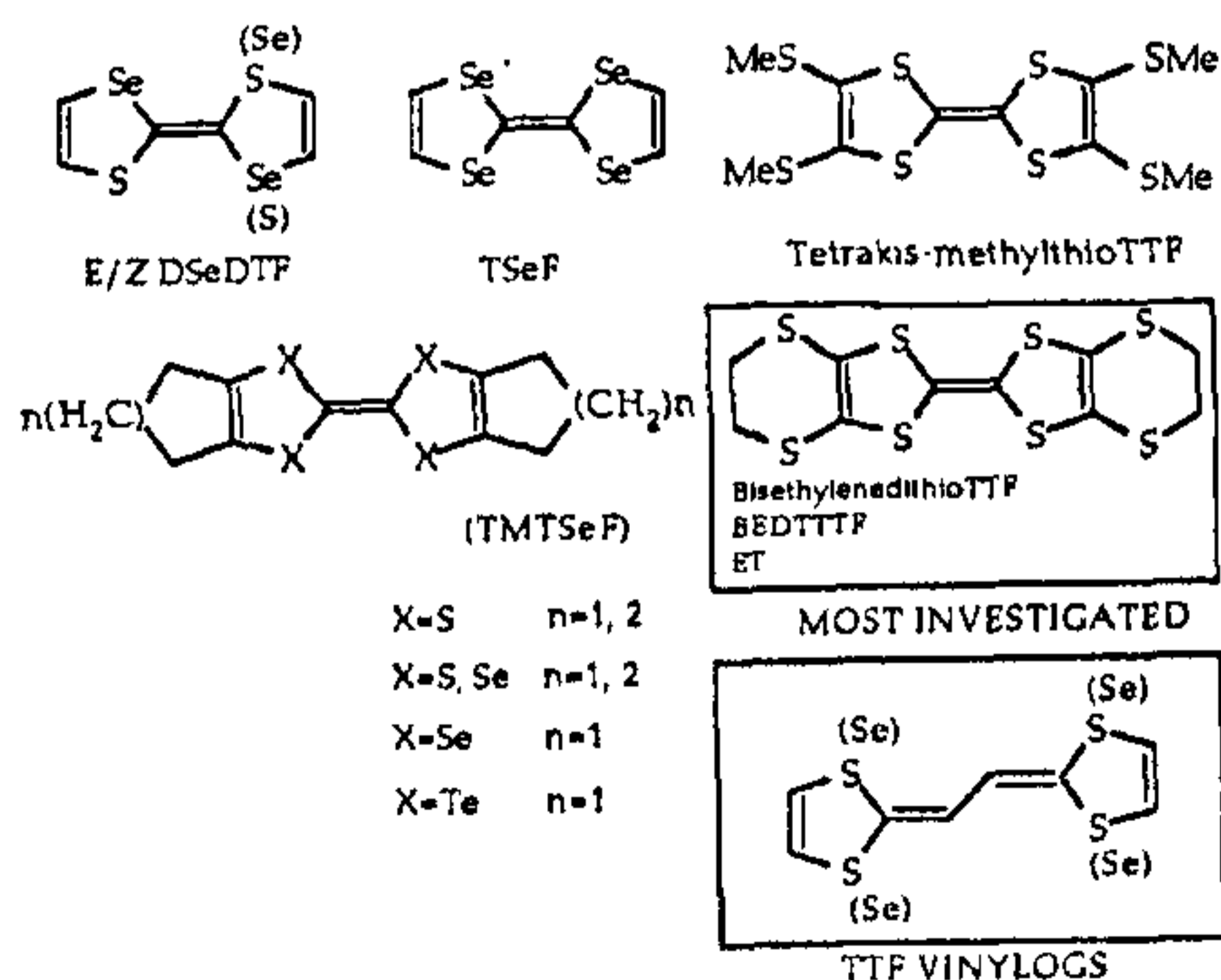
The impetus to the search for "organic metals" came in the early seventies with the discovery of one-dimensional conductivity exhibited by a charge-transfer complex formed by the action of tetracyanoquinodimethane (1) on tetrathiafulvalene (2)<sup>2, 3</sup>.



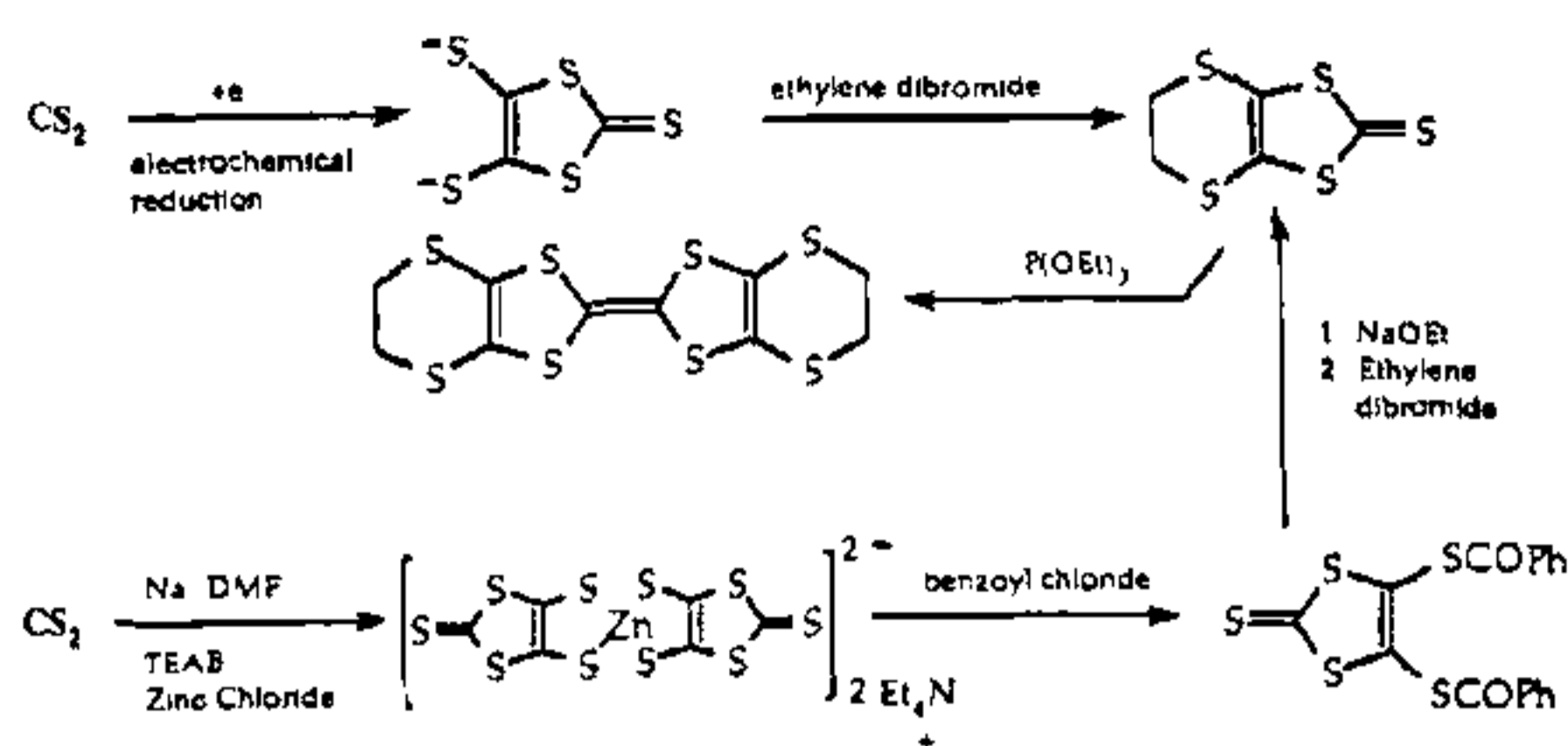
Soon many derivatives of 2 were made and before too long, it was found that not all of the C.T. complexes derived from them and 1 were electrically conducting. During the mid-seventies Engler<sup>4</sup> presented a simple model for the mechanism of one-dimensional electrical conduction.

The possibility of designing organic metals with analogs of TTF has attracted considerable attention. Some of the variants of 2 which we were interested in are shown in Scheme 1. In this series of molecules, bis-ethylenedithiotetrathiafulvalene (ET for short) was first synthesized in our group<sup>5</sup> as shown in Scheme 2.

The synthesis of ET has been considerably improved since then<sup>6</sup>. ET exhibited two reversible oxidation potentials at 0.49 V and 0.74 V and it gave a C.T. salt with



Scheme 1.



Scheme 2.

TCNQ whose conductivity at room temperature was  $50$  ( $\Omega \text{ cm})^{-1}$ .

Soon thereafter, it was discovered by Saito *et al.* that some salts of ET exhibited two-dimensional conductivity. Around the same time, in 1980 scientists in two labs reported independently that a cation radical fluorophosphate of tetramethyl tetraselenafulvalene exhibited superconductivity at 1 K under 12,000 atm<sup>7, 8</sup>. The perchlorate salt was the first ambient pressure superconductor with  $T_c$  of 1.2 K. In 1983, superconductivity was observed for the first time in an all sulphur donor derived salt viz (ET)<sub>2</sub>ReO<sub>4</sub> at 4,000 atm 1.4 K (ref. 9).

A triiodide salt of (ET)<sup>+</sup> has been reported to be superconducting at ambient pressure at 1.3–8 K (ref. 10). About this period in time, interest in polymeric conductors surfaced with the discovery of conducting behaviour by polyacetylene upon doping. During the last decade many polymers have been made and oxidized to give conducting materials. With all these advances a new picture of molecular conductivity emerged (Figure 1).

The above exciting results led to frenzied activity around the world to synthesize new  $\pi$ -electron donor molecules based on known prototypes. In the next section, chemical precedents to the synthesis of numerous variants of TTF are discussed. This is followed by a summary of work done in our laboratory on the synthesis and electrochemical properties of several novel donors.

### Variants of TTF

In 1861, Hofmann<sup>11</sup> reported the reaction between carbon disulphide and tri-butyl phosphine to give red adduct. In 1971, Hartzler<sup>12</sup> showed that this adduct reacted with a mixture of benzaldehyde and dimethyl acetylene dicarboxylate at  $-78^\circ\text{C}$  to give 3, a dithiafulvene, via a Wittig-type reaction. In 1979, Gonnella *et al.*<sup>13</sup> trapped the intermediate phosphorane with acid to give a stable crystalline salt 4, which reacted with aldehydes at room-temperature in the presence of triethylamine to give dithiafulvenes (Scheme 3).

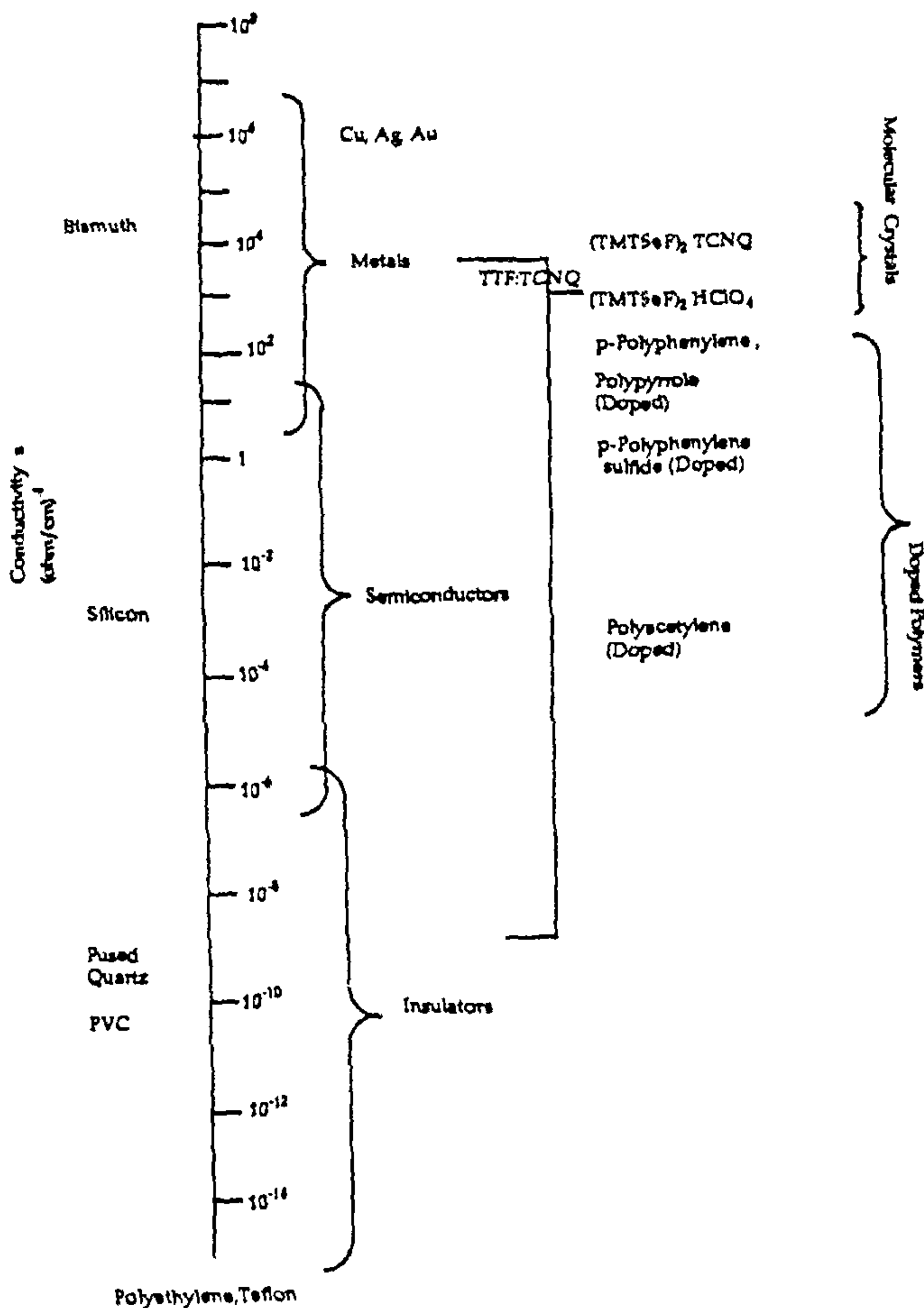
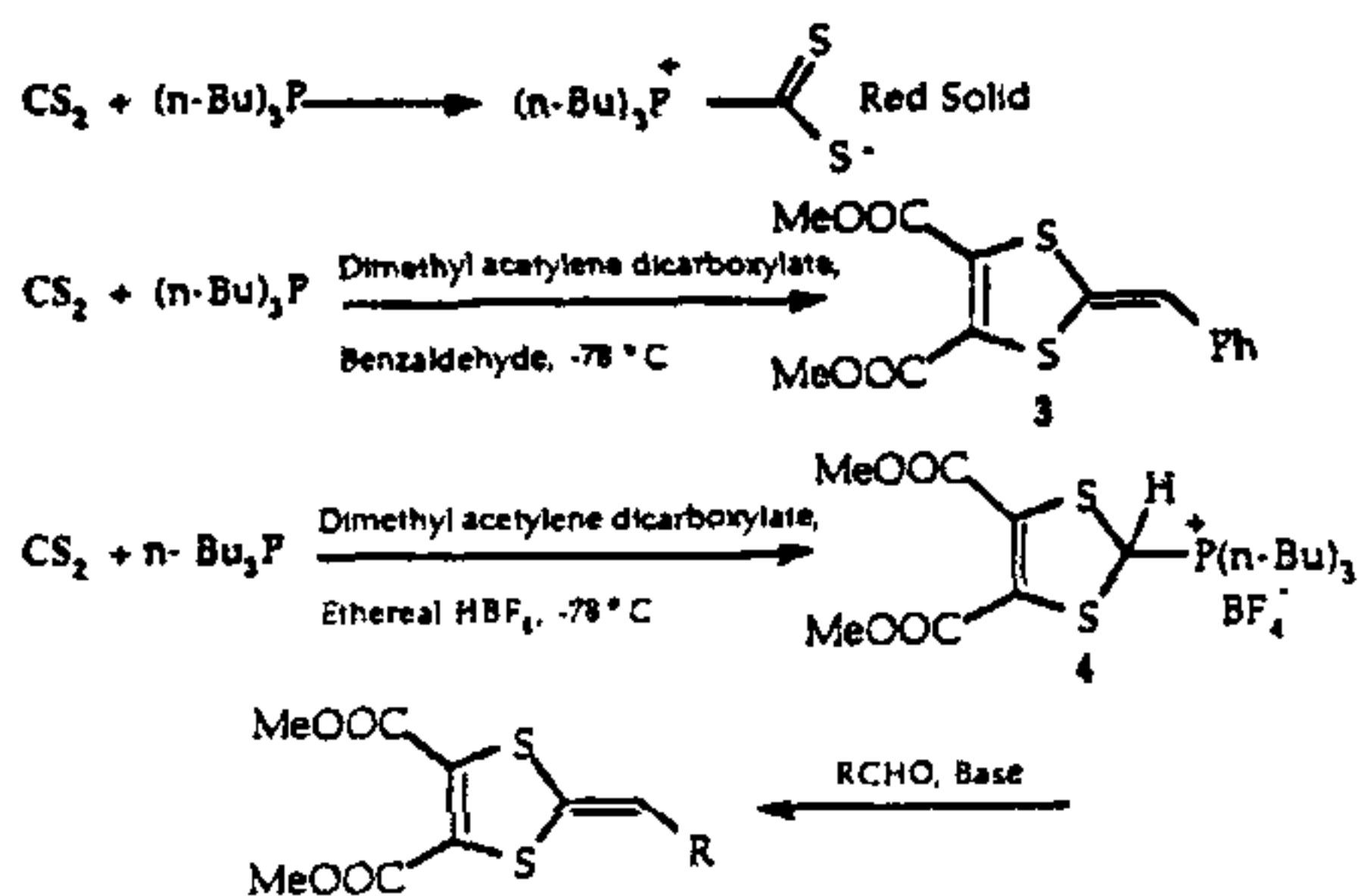


Figure 1. Comparison of conductivity of materials.

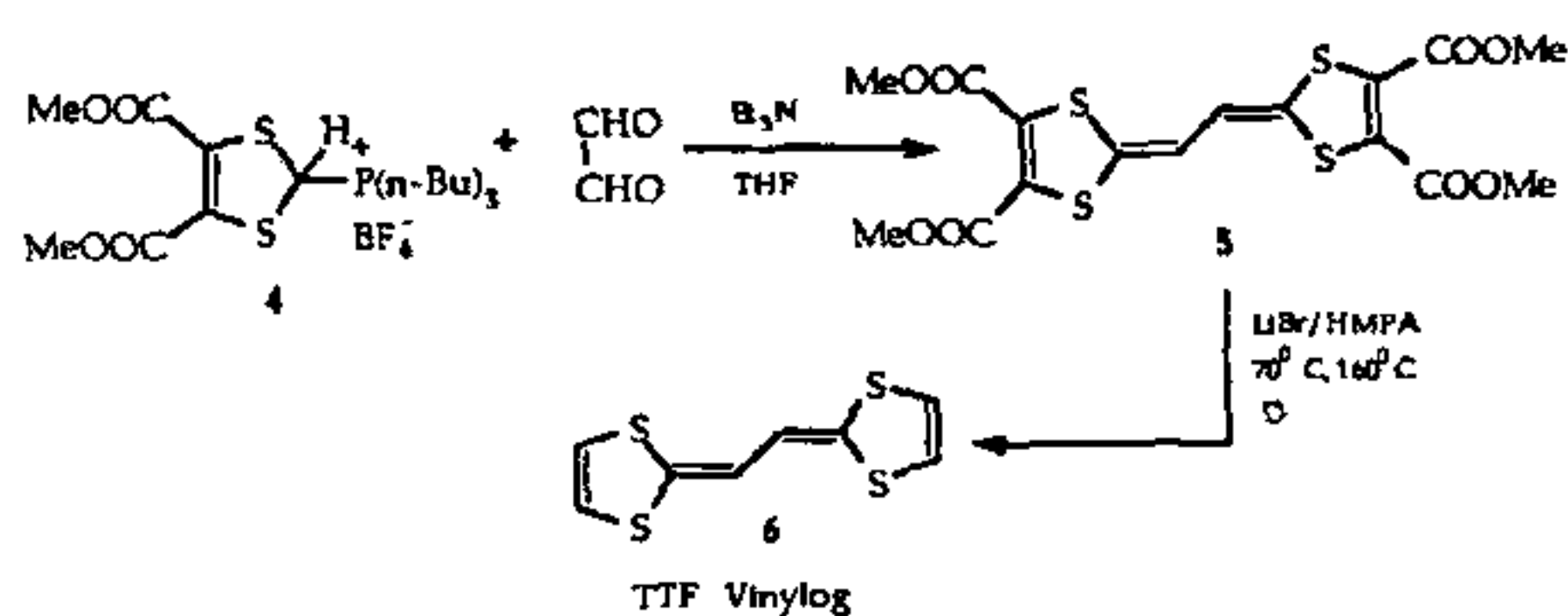
In 1983, Yoshida *et al.*<sup>14</sup> prepared the first vinyllogous TTF by reacting glyoxal with the ester phosphonium salt 4 described above. The resulting vinyllogous TTF tetraester 5 was decarbomethoxylated to the TTF vinyllog

6 by the use of LiBr/HMPT, by a previously described process<sup>15</sup> (Scheme 4).

The diseleno analog 7 was prepared by an alternate procedure<sup>16</sup> as shown in Scheme 5.

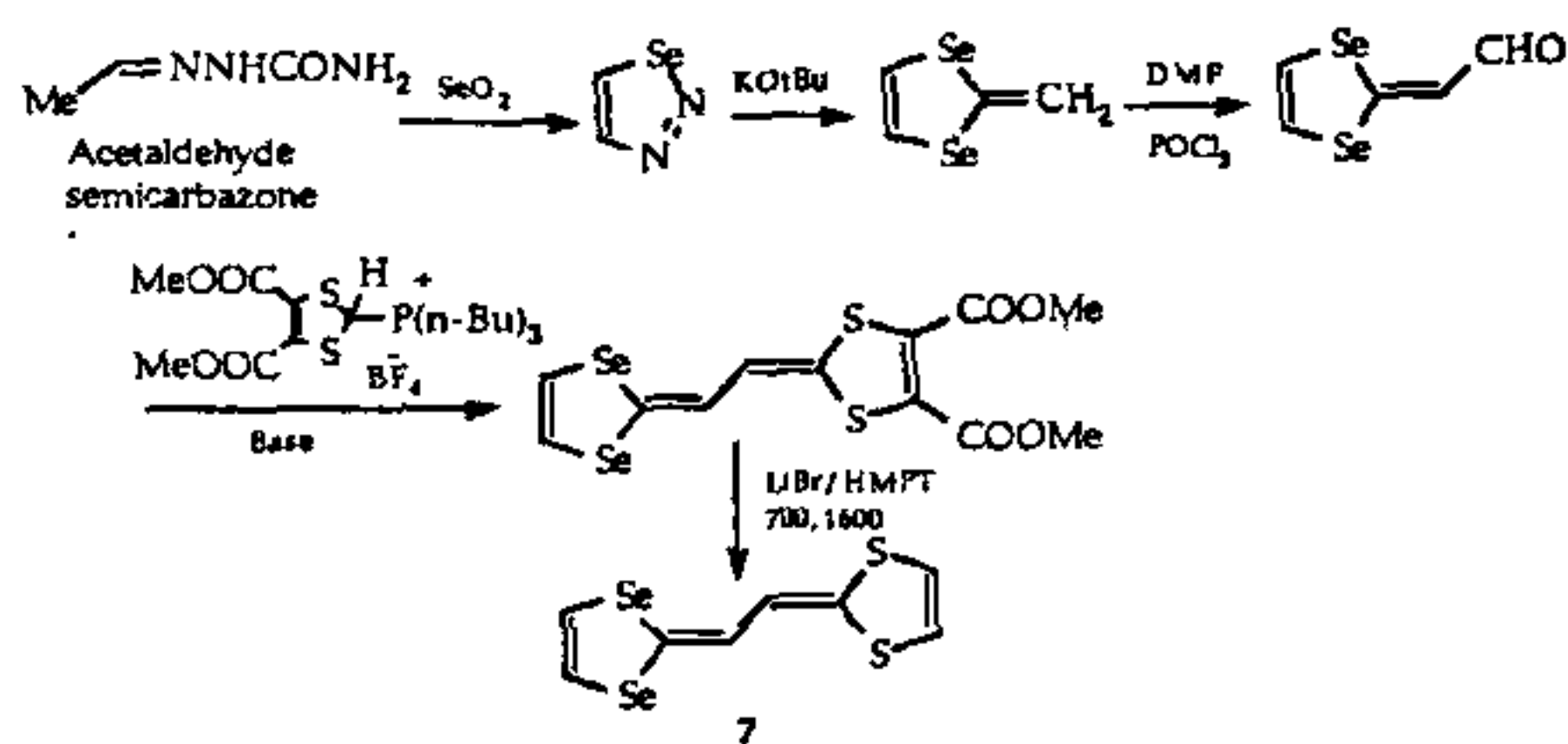


Scheme 3.



Scheme 4.

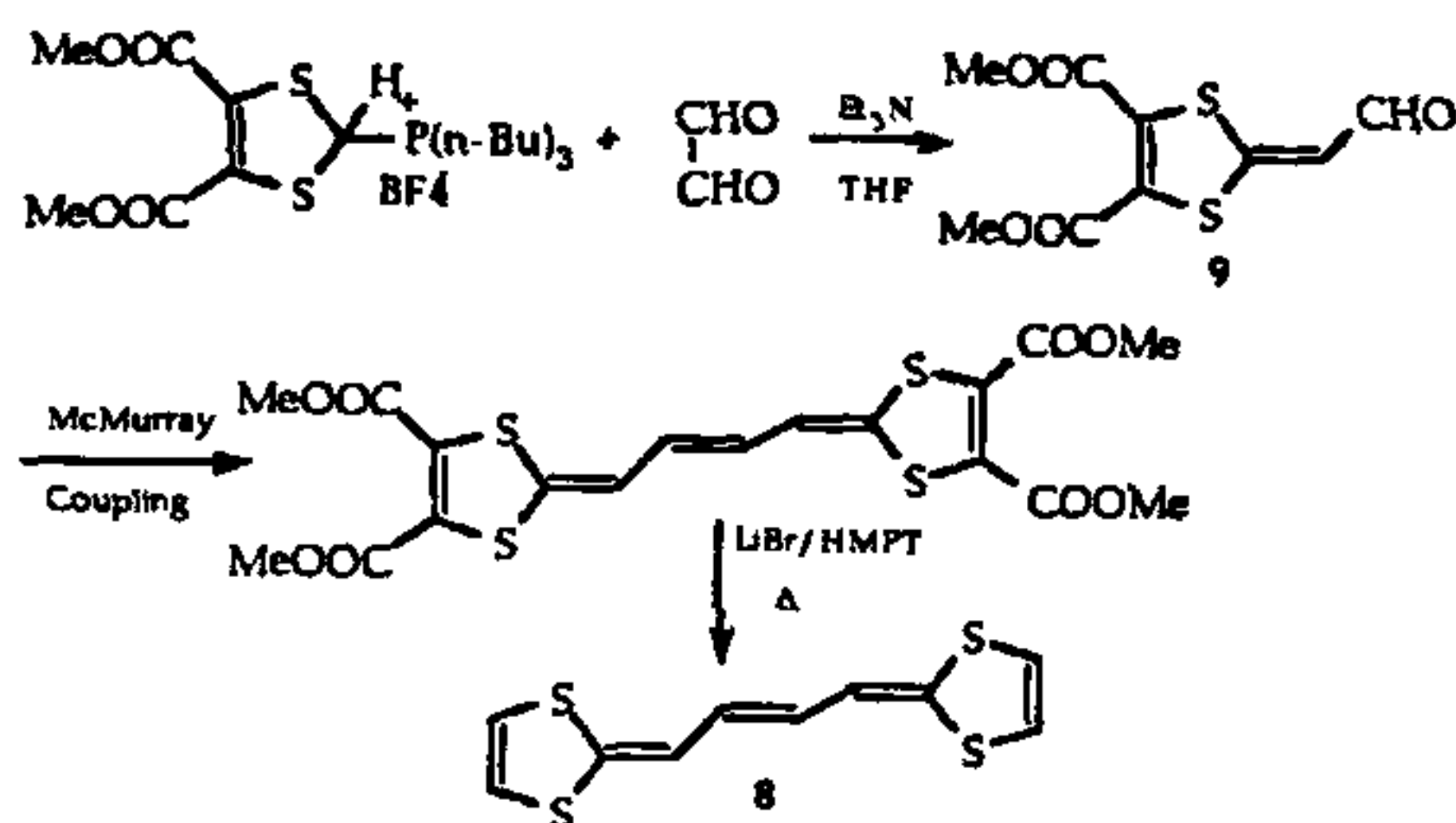
The diselenena analog **7** was prepared by an alternate procedure as shown in Scheme 5.



Scheme 5.

Yoshida *et al.*<sup>17</sup> also prepared an extended vinylog **8** by a McMurry-Type coupling of an intermediate aldehyde **9** as shown in Scheme 6.

A comparison of the C.V. data of the vinylogs and TTF showed that  $E_2 - E_1$  was smaller ( $\sim 0.14$ – $0.16$  V) than that in TTF (0.38 V) (Table 1). Even more interesting was the observation that when the dithiolenic units were separated by three double bonds as in **8**,  $E_2 - E_1$  practically vanished, only one oxidation wave being discernible at 0.2 V.



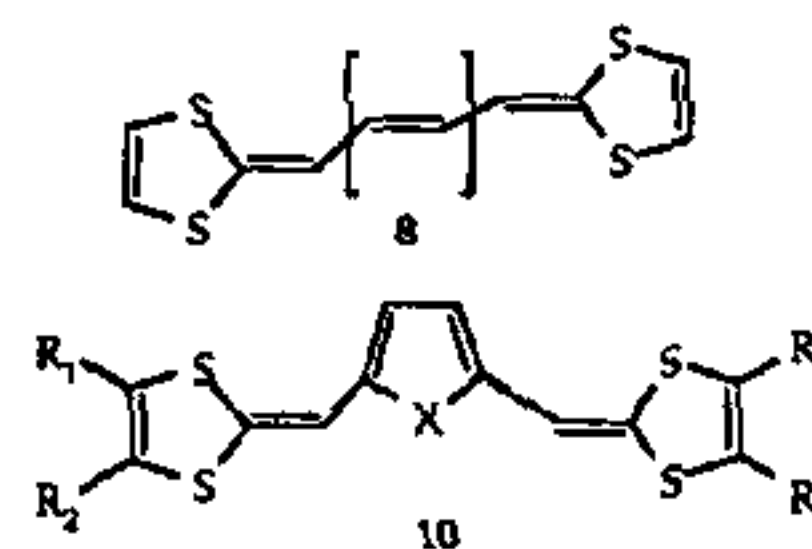
Scheme 6.

Table 1. Cyclic voltammetry data on TTF and vinylogs

	$E_1$ (V)	$E_2$ (V)	$E_2 - E_1$ (V)
	0.33	0.71	0.38
	0.20	0.36	0.16
	0.26	0.40	0.14
	0.33	0.47	0.14

Solvent MeCN; Electrolyte 0.1 M TEAP; Electrode Ag/AgCl.

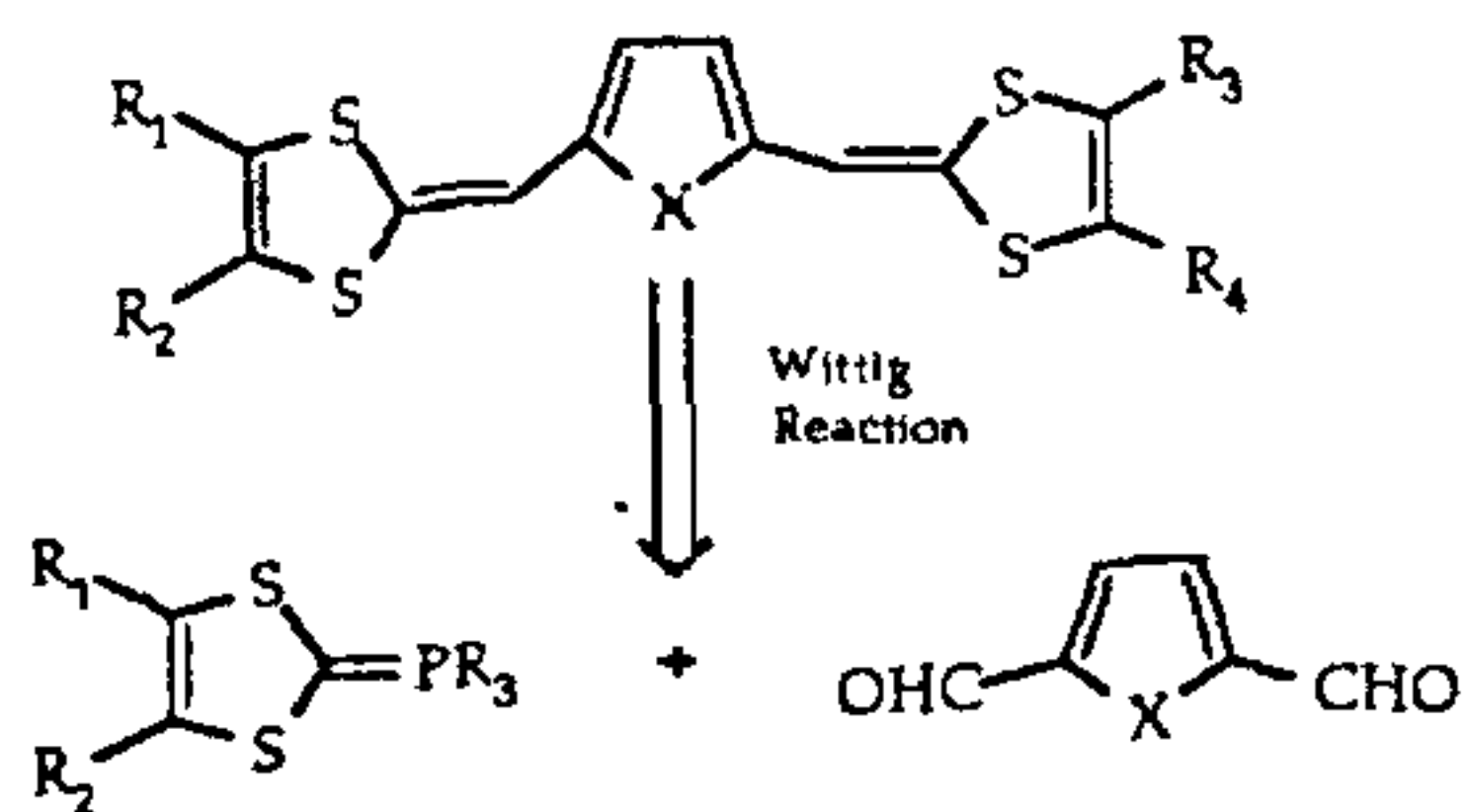
Our studies focused on the modification of the structure **8**, by the replacement of the central double bond by common heteroaromatic rings and a study of the electrochemical oxidation of the resulting molecule **10**. (Scheme 7).



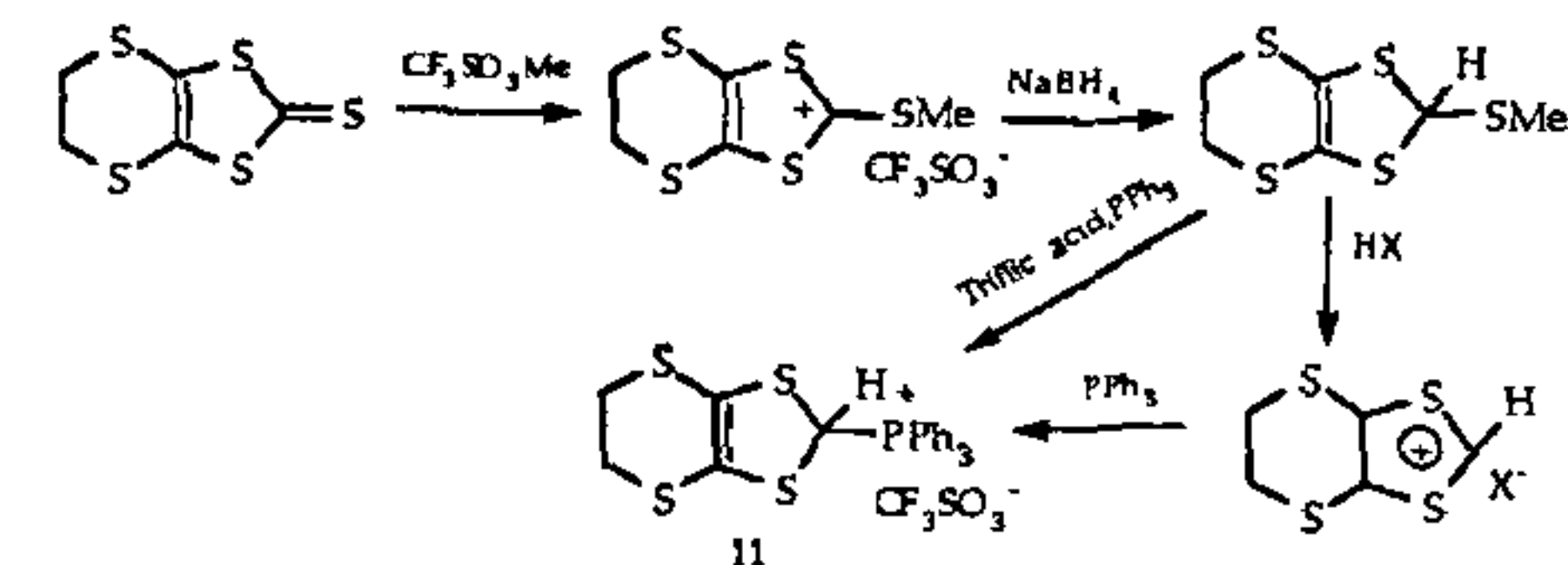
Scheme 7.

The general approach was based on the tried and tested Wittig reaction between the appropriate dialdehyde and the corresponding phosphoranes (Scheme 8). The 1,3-dithiolenic phosphonium salts **11** and **12** were prepared by procedures developed in our labs<sup>18,19</sup> (Scheme 9).

The diester phosphonium salt **4** condensed with furan, N-methyl pyrrole and thiophene 2,5-dialdehydes<sup>20,21</sup> in acetonitrile in the presence of triethylamine at room

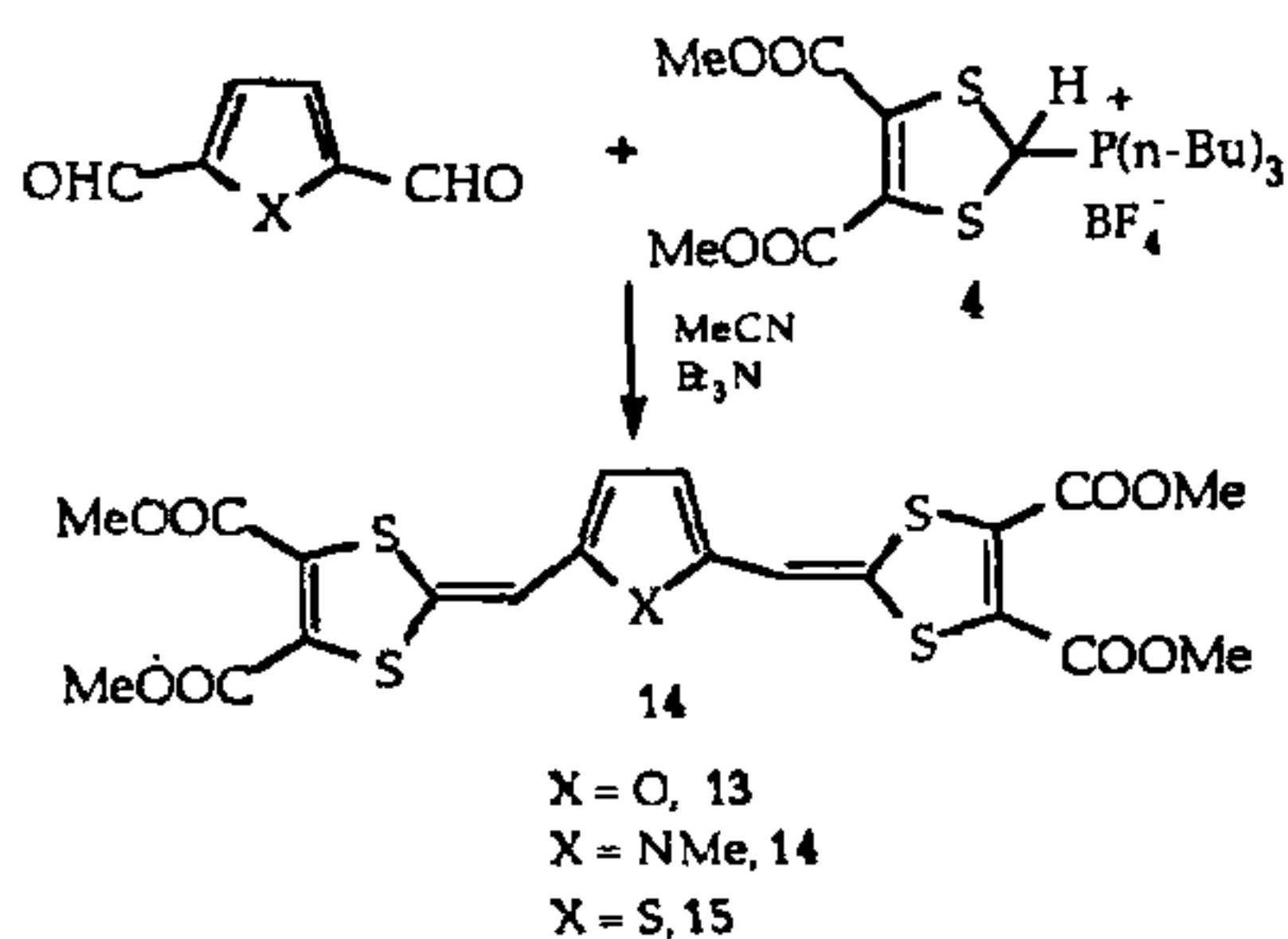


Scheme 8.



Scheme 9.

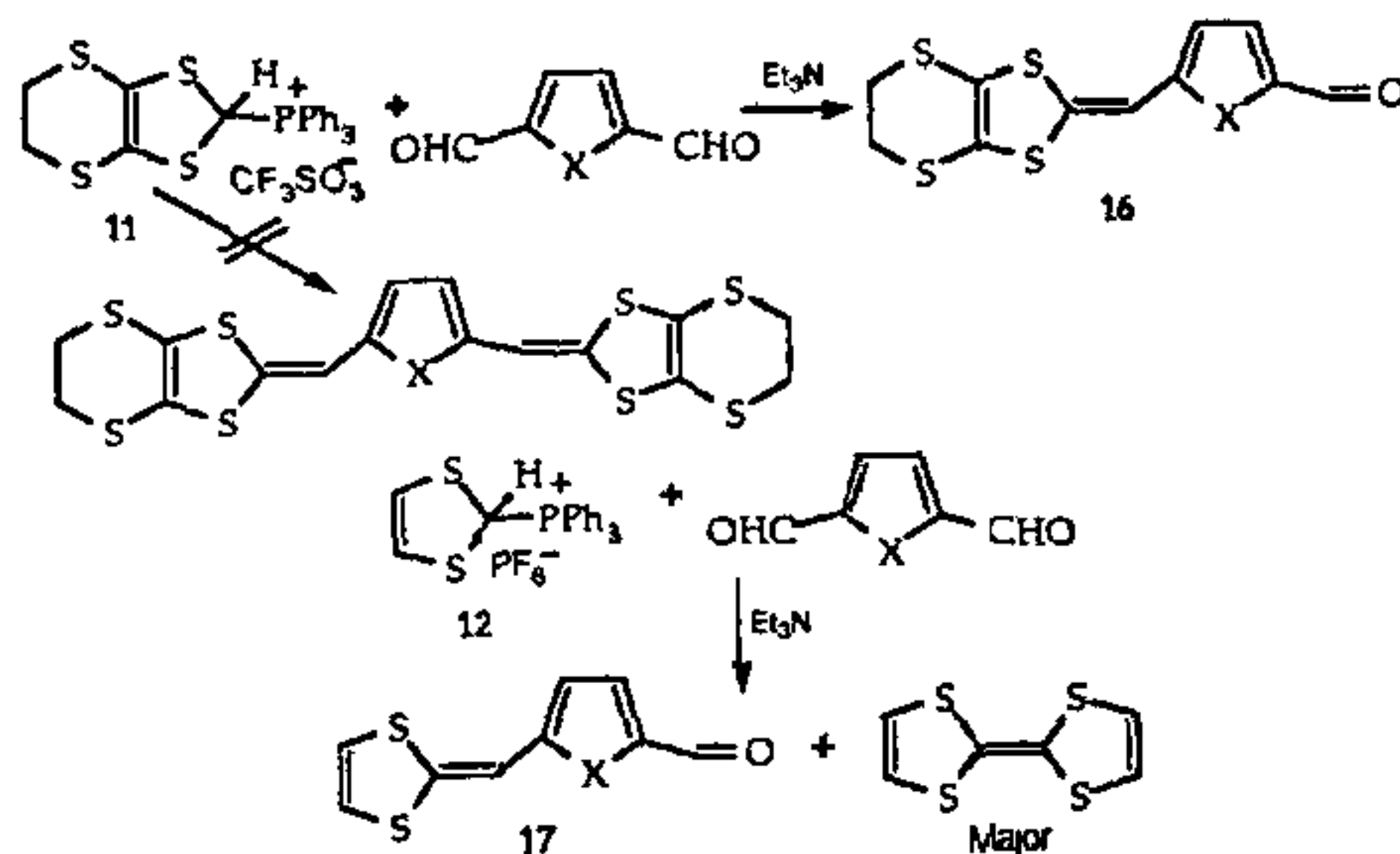
temperature to give the expected products **13–15** in high yield<sup>22</sup> (Scheme 10).



Scheme 10.

The ethylenedithia phosphonium salt **11** did not give the expected product under analogous reaction conditions, but gave an intermediate aldehyde **16**. The simple phosphonium salt **12** gave TTF as the major product with very small amount of the intermediate product **17**

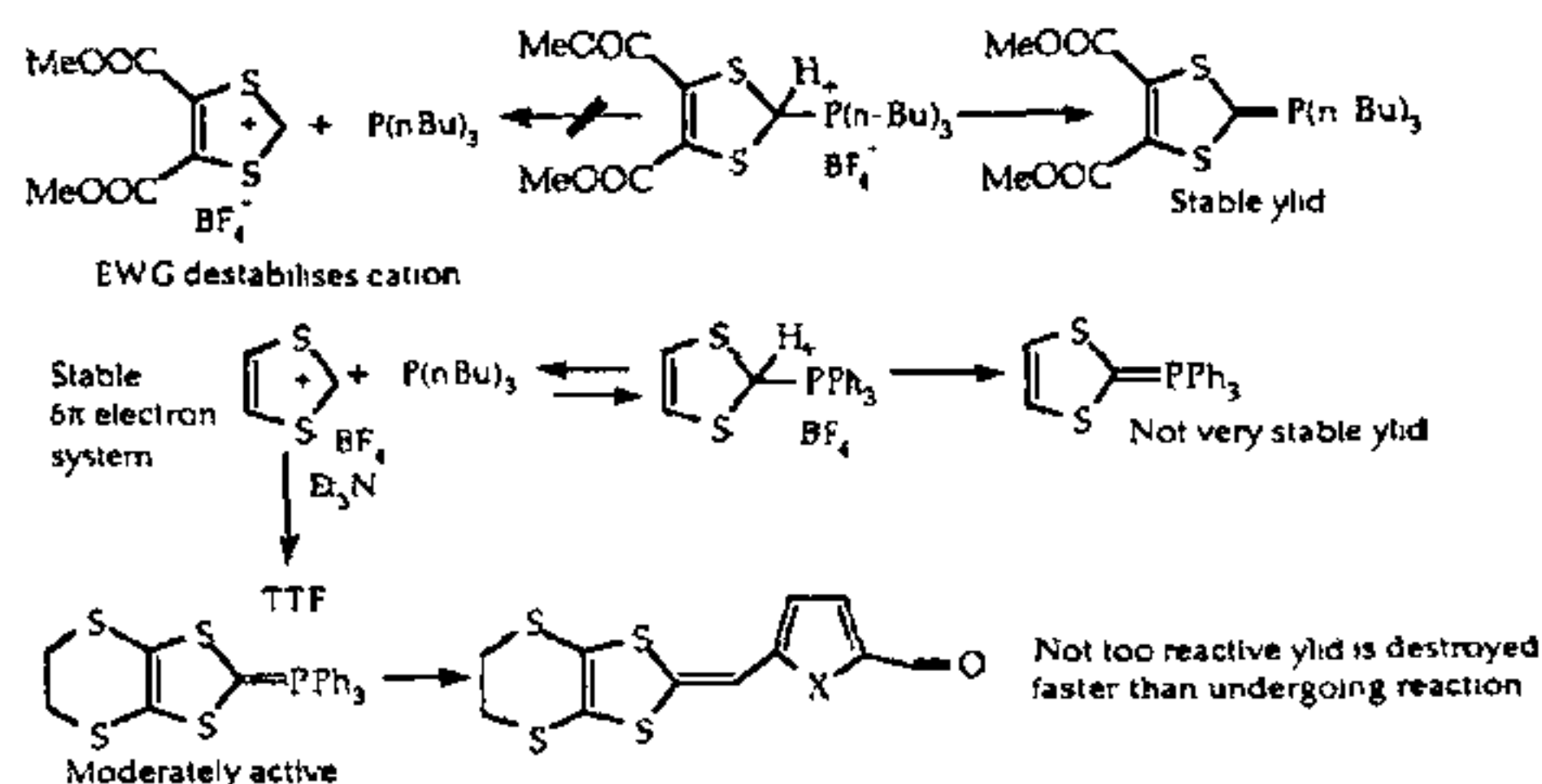
(Scheme 11). The cause of this failure can be explained on the basis of the stability of the intermediate yields in these reactions. The simple yield incorporates a 8 π electron antiaromatic system which therefore is not



Scheme 11.

a very stable yield. Furthermore, the phosphonium salt is in equilibrium with its parent components. The simple yield must therefore be formed slowly and in the absence of highly reactive aldehydes, it can fragment and be destroyed. The simple thiolium salt generated in the equilibrium therefore is deprotonated faster than yield formation and it is transformed into TTF. The yield derived from the dithiaethylene analog **11** is moderately stable although it is formally also a 8 π electron system, because it cannot readily fragment destructively. The diester phosphonium salt **4** in contrast to these cannot revert to the parent components and the yield generated from it is also stabilized by the electron withdrawing groups on the dithiole ring (Scheme 12).

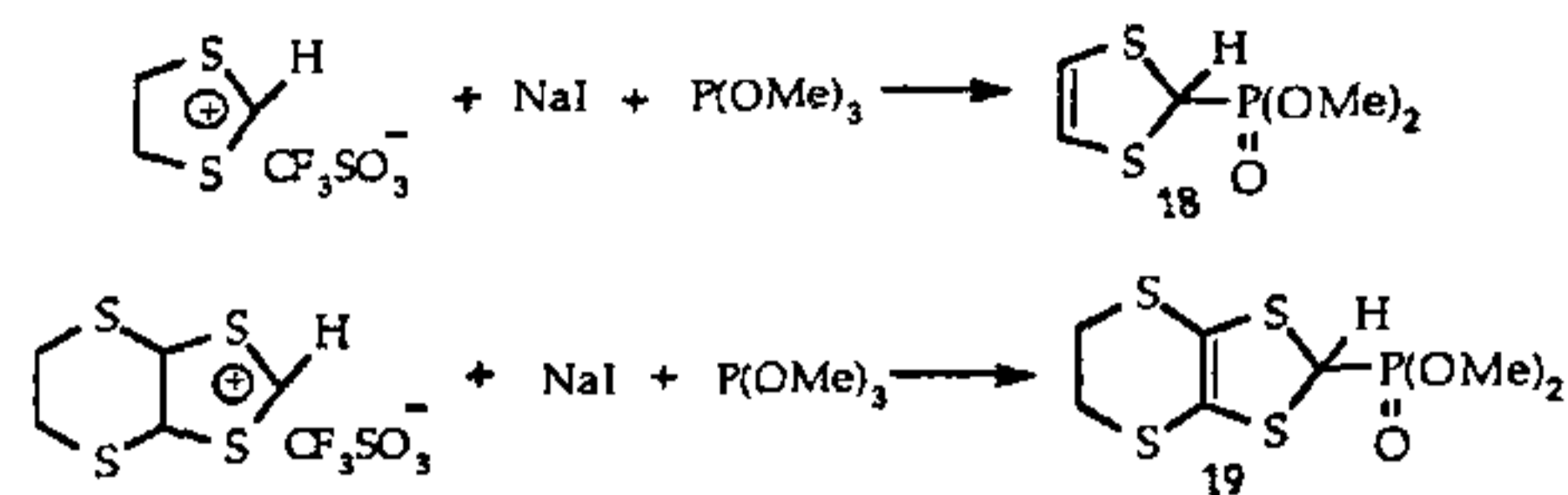
In order to overcome the problems encountered, phosphonates **18** and **19** were prepared from the respective



Scheme 12.

thiolium salts and trimethyl phosphite (Scheme 13), so as to use the Horner-Wittig modification.

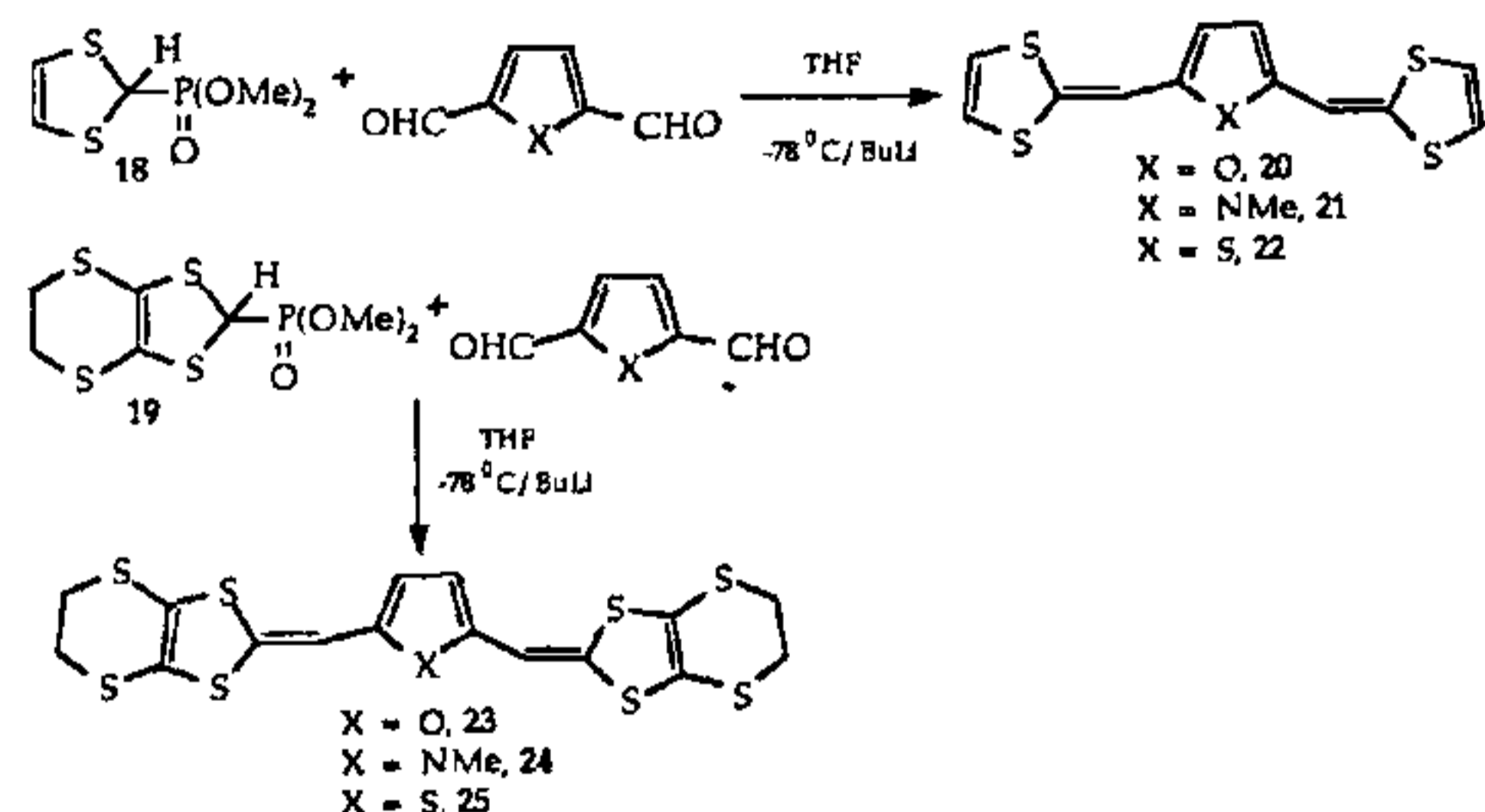
Deprotonation of the phosphonates **18** and **19** was carried out at  $-78^{\circ}\text{C}$  in tetrahydrofuran solution using



Scheme 13.

BuLi, followed by reaction with the 2,5-dialdehydes from furan, N-methyl pyrrole and thiophene. The extended TTF derivatives **20** and **21** were obtained in generally low yields from furan and N-methyl pyrrole dialdehydes. Thiophene dialdehyde provided a modest yield of the extended TTF **22**. In contrast, the yield from phosphonate **19** gave a 66% yield of product (**23**) from furandialdehyde and an 87% yield of **24** from N-methyl pyrroledialdehyde. Thiophenedialdehyde gave a modest yield (51%) of product **25** (Scheme 14).

The nine extended TTF analogues (**13–15**, **20–25**) can be viewed as two dithiolenes connected by four double bonds, if one were to ignore the hetero atom.



Scheme 14.

One can then expect by analogy to the behaviour of **8**, which has three double bonds separating the dithiolenes, that there should be no difference between  $E_1$  and  $E_2$  in their C.V. However, except in the case of the simple furan derivative **20**, all the others showed two distinct oxidation waves. Furthermore,  $E_2 - E_1$  was the lowest in all the other furan derivatives. These results clearly show the strong influence of the hetero atom and the involvement of the heteroaromatic ring in the oxidation process. It was also remarkable that the

tetraester derivatives **13–15** showed  $E_1$  of 0.48–0.69 V in comparison to  $E_1 = 0.78$  V shown by TTF tetraester derivative **26** (Table 2).

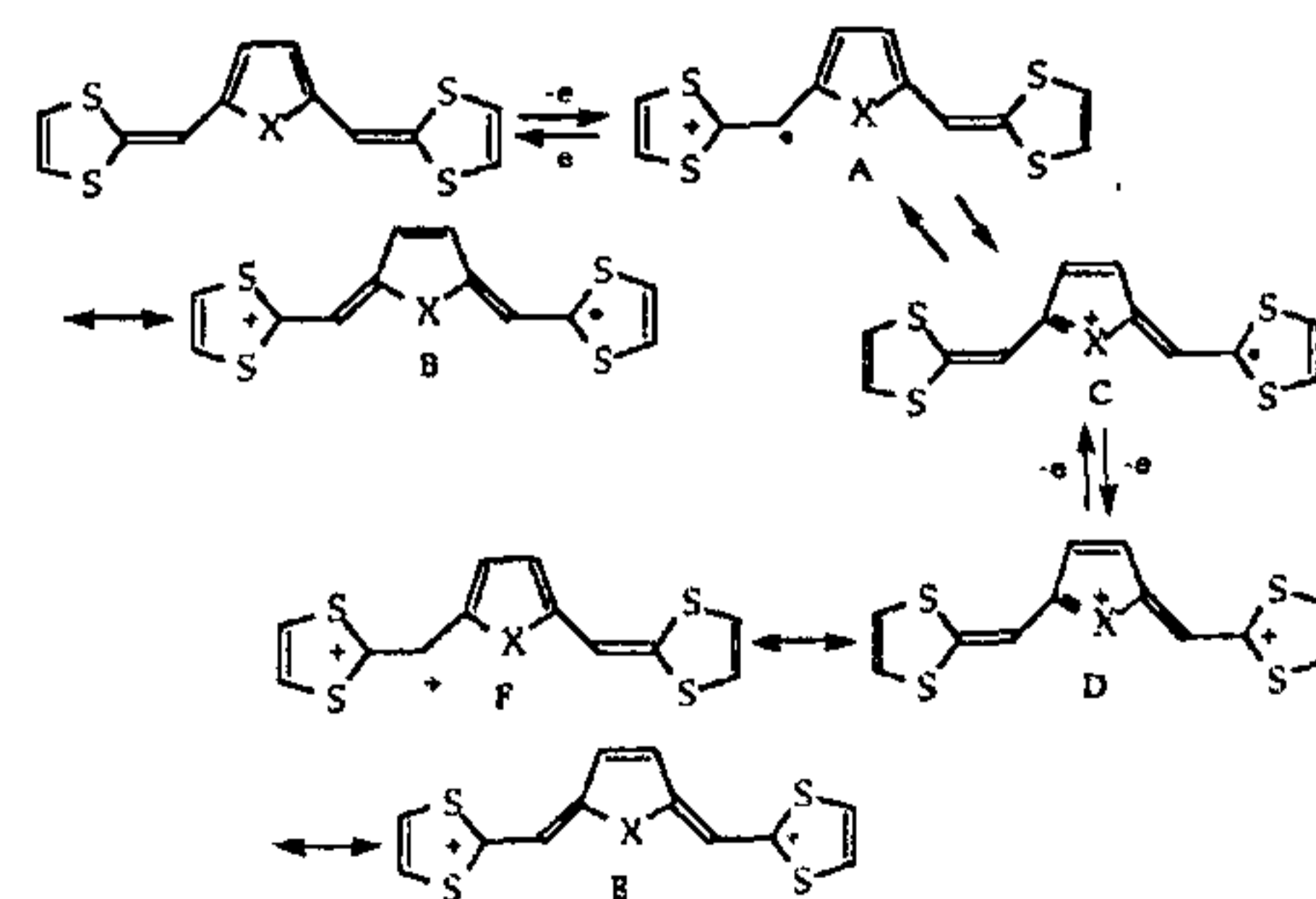
Let us consider the resonance structures in the radical cations and diradicals in these extended TTF derivatives with heterocyclic spacers (Scheme 15).

Structure A contains an intact heteroaromatic ring, a stable thiolium ring and a benzylic radical and must be a major contributor. In contrast, structure F, must be a negligible contributor, although it has an intact heteroaromatic ring and a dithiolenium system because of severe repulsion between adjacent positive charges.

Structures such as C and D incorporate a positively charged heteroaromatic spacer. The importance of such structures should follow the order pyrrole > furan > thiophene; in view of the fact that nitrogen bears a positive charge better than oxygen or sulphur. This is

Table 2. Comparison of C.V. data for the extended  $\pi$ -donor

X	$E_1$ (V)	$E_2$ (V)	$E_2 - E_1$ (V)
	0.32		0.0
NMe	0.2	0.38	0.18
S	0.39	0.49	0.10
	0.38	0.56	0.18
NMe	0.31	0.58	0.27
S	0.46	0.65	0.19
	0.58	0.71	0.13
NMe	0.48	0.81	0.23
S	0.69	0.79	0.10
	0.33	0.71	0.38
	0.78	1.1	0.33



Scheme 15.

reflected in the highest value for  $E_2 - E_1$  in the pyrrole series in all three cases.

Contributors **B** and **E** do not have an aromatic spacer group. Such loss of aromaticity can be better tolerated in the furan series than in the pyrrole or thiophene series. However, these contributors are expected to be of increasingly higher energy and therefore perhaps less important.

Two complexes with TCNQ were made from **13** and **20**. Two-probe conductivity measurements were made. The complex from **13** showed  $\sigma = 10^{-2} (\text{ohm/cm})^{-1}$  and the one from **20** had  $\sigma = 10^{-5} (\text{ohm/cm})^{-1}$ . It is remarkable for a  $\pi$ -donor bearing an EWG as in **13** to give a conducting complex since the simple TTF tetraester **26** has a high  $E_1$  and does not give any complex with TCNQ.

### Summary

Since the discovery of the electrical conductivity of TTF-TCNQ complex in 1973, literally hundreds of variations on the basic structure of the molecule have been carried out. During the course of the last decade or so, the discovery of superconducting properties of some salts derived from the  $\pi$ -donor ET has further triggered tremendous synthetic endeavours<sup>23</sup>. While a lot of information is available, it is paradoxical that no absolute prediction can be made about the electrical properties of the  $\pi$ -donors or complexes or salts derived from them. There is still a lot of potential in this area, since the ultimate goal of R.T. superconductivity has not been reached.

The work described here is but one small variation on a basic structure exhibiting  $E_2 - E_1 = 0$ . The perturbation of this structure with common heterocyclic rings has changed the C.V. behaviour of the new donors considerably.

While it is generally accepted that EWG on the donors lead to poor oxidation properties, the first good donor with -COOMe groups is like TTF in its C.V. behaviour and has been shown to yield a TCNQ complex with conducting properties. Further work in this area is in progress in our labs.

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