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Synthesis Of Unsymmetrically Substituted TTF Derivatives *Via* The "Phosphonate Way". Some Investigations On The Scope Of The Method.

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Abstract: The scope and limitations of the synthesis of unsymmetrically substituted TTF derivatives *via* the "phosphonate way" was investigated using as precursors 1,3-dithiol-2-yl-phosphonates and 1,3-dithiol-2-yliden iminium salts with various substituents on the dithiole cycles.
Except for the un- or monosubstituted phosphonates, the one-pot procedure proves to be general and affords in all cases a significant improvement in the overall yields in TTF derivatives.
The study has shown also that the formation of the intermediate adducts occurs in high yield, but their transformation into TTF derivatives, in presence of anhydrous acetic acid, is strongly sensitive to the nature of the various substituents, particularly on the iminium part.

Introduction.

The unsymmetrically substituted TTF derivatives are particularly interesting as precursors for the preparation of organic conductors, and even superconductors.[1]

Of course, extending some convenient syntheses of symmetrically substituted TTF derivatives, the cross-coupling of two appropriate dithiolium salts,[2,3] as well as 2-oxo, 2-thioxo, or 2-selenoxo 1,3-dithioles [4] can be used to obtain such unsymmetrically TTF derivatives. However these methods exhibit a low selectivity and they involve the necessary separation of the unsymmetrical TTF derivatives from the resulting two symmetrical species concomitantly formed in the reaction.

Several synthetic pathways have also been developed to obtain selectively the unsymmetrical structures from two different kinds of precursors. They involve: (i) the reaction of a metalated TTF derivative with various electrophiles,[5] (ii) the reaction of lithiated orthotrithioesters with 2-thioxo-1,3-dithioles,[6,7] (iii) the reaction of an 1,3-dithiol-2-yl phosphonium ylide with a dithiolium salt[8-11]; (iv) the reaction of organotin chalcogenolates with dithiole esters;[12] (v) the reaction of an 1,3-dithiol-2-ylphosphonate carbanion with an 1,3-dithiol-2-ylidene iminium or sulfonium salt.[13]. The last method seems to be easy, general and fully selective. Accordingly, in connection with our interest in the synthesis of unsymmetrically substituted TTF derivatives, we recently investigated thoroughly the reaction between the diethyl 2-[4,5-benzo-1,3-dithiol-2-yl]phosphonate carbanion **1'**, and the 4,5-dimethyl-1,3-dithiol-2-yliden piperidinium hexafluorophosphate **2** to afford the adduct **3** which is then deaminated and dephosphorylated

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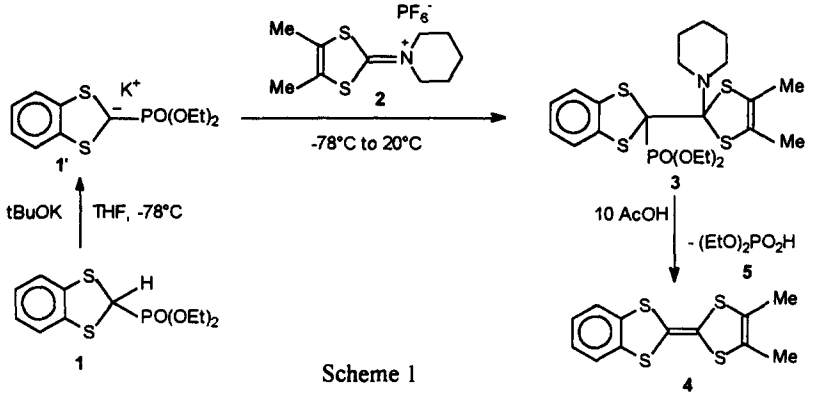
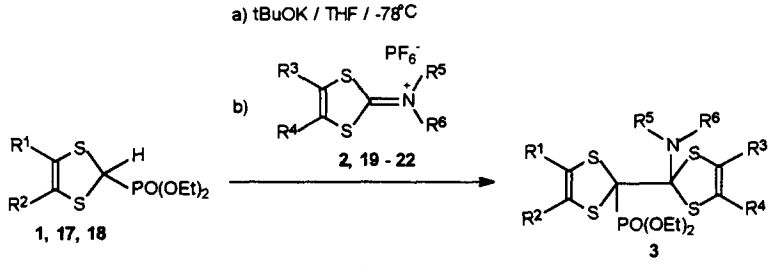
into the TTF derivative **4** by means of anhydrous AcOH (scheme 1). As a result of our mechanistic investigations we developed an improved procedure using a ratio ρ = [AcOH] / [phosphonate] = 10 (with [phosphonate] = 6.89 10^{-3} mol.L^{-1}) to give in high yield the expected TTF derivative **4**.[14]



Scheme 1

This result encouraged us to study the scope and limitations of this two-step "one-pot" procedure by changing the structure of the starting phosphonates and iminium salts for the preparation of various unsymmetrical TTF derivatives (scheme 2, table 1).



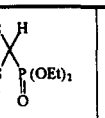
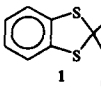
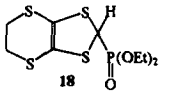
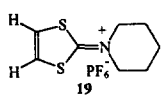
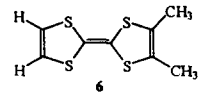
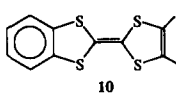
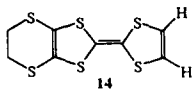
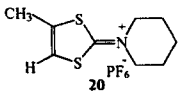
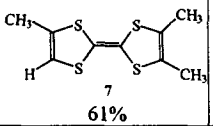
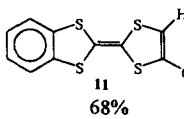
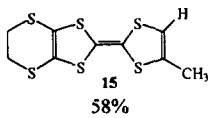
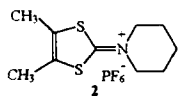
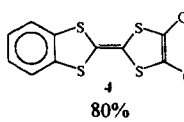
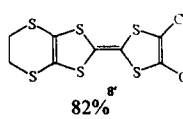
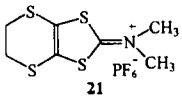
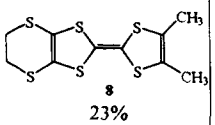
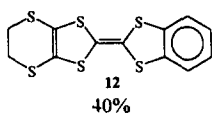
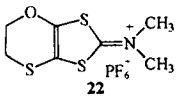
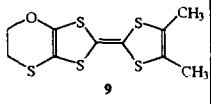
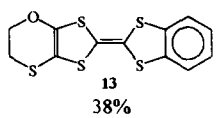
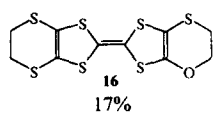
Scheme 2

In the phosphonates **1**, **17**, and **18**, the dithiole ring is respectively disubstituted by alkyl, aryl or heterocyclic groups. It is noteworthy that we also investigated unsubstituted (R^1 = R^2 =H) and monosubstituted structures (R^1 = H, R^2 = Me), but they display an unexpected behaviour which will be separately published.

Concerning the iminium salts **2** the dithiole ring is either unsubstituted (**19**), monosubstituted (**20**)- or disubstituted by alkyl (**2**) or heterocyclic substituents (**21, 22**) and the R^5 and R^6 nitrogen substituents proceed from piperidine or from dimethylamine.

Most of the unsymmetrical TTF derivatives **4**, **6 - 16** are known, or the unfructuous attempts for their synthesis were published . As indicated in Table 2, all the expected TTF derivatives were obtained in satisfactory overall yields corroborating the efficiency of our procedure. Indeed, in all cases we have increased the yields of TTF derivatives, in comparison with the results described in the literature.

Table 1: Yields of synthesized "unsymmetrical" TTF derivatives and their precursors.

Iminium Salts \ Phosphonates	 17	 1	 18
 19	 6 58%	 10 79%	 14 50%
 20	 7 61%	 11 68%	 15 58%
 2		 4 80%	 82%
 21	 8 23%	 12 40%	
 22	 9 40%	 13 38%	 16 17%

Further, as the synthesis of unsymmetrical TTF derivatives *via* the "phosphonate way" is a two step procedure, besides the overall yields in TTF derivatives, we also determined both the formation yields of the intermediate adducts (first step) and of the TTF derivatives (second step), in order to identify the limiting step in a possible less satisfactory synthesis (like **8** or **16** for exemple).

Concerning the first step, the formation yields were determined by ^{31}P-NMR spectroscopy. As indicated in table 2, the adducts **23** are quantitatively formed from the piperidino-iminium salts **2**, **19**, **20**, with or without alkyl substituents on the dithiole ring, whatever the phosphonate used. But in the case of dimethylamino-iminium salts **21**, **22**, with heterosubstituents on the dithiole ring, the yields of formation of the corresponding adducts **23** lie only between 77 and 89%. Accordingly the nature of the substituents R^5, and R^6 on the nitrogen and/or R^3, R^4 on the dithiole ring of the iminium salts play a role in the formation of the adducts **23**. Likely, the mesomeric donor effects of the heteroatomic substituents $R^3$and R^4 in the iminium salts **21** or **22** decrease their electrophilic character, resulting therefore in lower yields for the formation of the corresponding adducts. But, nevertheless, the first step of the synthesis, with an average yield of 89% for the thirteen examples shown, can not be considered as a limiting step.

Table 2: Comparison between the yields obtained in the synthesis of TTF derivatives and the data of the literature.

Starting compounds		Adducts 23	TTF derivatives			
Phospho-nates	Iminium Salts	Yd. (%)[a]	Compd.	Yd. (%)[b]	Yd. (%)[c]	Yd. (%)[d]
1	**2**	100		92	80	30,[7] 80,[8,10] e)[16]
17	**19**	100	**6**	69	58	25[3]
17	**20**	100	**7**	78	61	40[11], 49[17]
17	**21**	77	**8**	23	17	e)[17,18,19]
18	**2**	100	**8'**	82	74	e)[17]
17	**22**	83	**9**	54	40	38[20]
1	**19**	100	**10**	89	79	40[8], 29[21], 31[22]
1	**20**	100	**11**	89	68	
1	**21**	79	**12**	55	40	14[23]
1	**22**	89	**13**	53	38	27[20]
18	**19**	100	**14**	68	50	35,[24] e)[17,18]
18	**20**	100	**15**	67	58	25[24]
18	**22**	88	**16**	27	17	0[20]

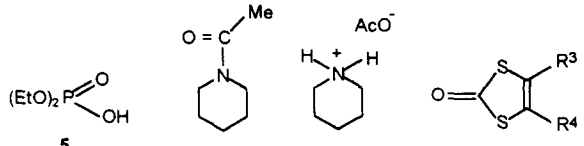
a) Yield of formation calculated from ^{31}P-NMR spectra: The adduct exhibits a characteristic signal with a chemical shift at about 15-16 ppm; b) Yield of formation calculated from ^{1}H-NMR spectra (using dibenzyl ether as internal reference); c) Yield of isolated pure compound; d) Yield reported in the literature according to the corresponding reference; e) Unspecified yield.

Further, concerning the second step of the synthesis, that is to say the decomposition of the adducts **23** into the corresponding TTF derivatives by addition of 10 equivalents of AcOH, the conversion yields were determined from ^{1}H-NMR spectra of the crude reaction mixture, after the complete disappearance of the adduct in the ^{31}P-NMR spectra. As indicated in table 2, the transformation is never quantitatively selective, and the yields of TTF derivatives can greatly vary from 23% to 92%. As for the adducts formation, their transformation into the TTF derivatives depends greatly on the starting iminium salts, and in this step more likely on the R^5 and R^6 nitrogen substituents. Indeed, the piperidino adducts are converted into the TTF derivatives **4**, **6**, **7**, **8**, **10**, **11**, **14**, and **15** in 67 – 92% yields whereas the dimethylamino adducts afford the TTF derivatives **8**, **9**, **12**, **13**, and **16** in only 23-55% yields. Particularly demonstrative for the contrast between piperidino and dimethylamino adducts, in the second step of the synthesis, is the comparison between the transformations resulting respectively in the same TTF derivative **8'** (82% yield) and **8** (23% yield). One explanation for the different behaviours of the two amino groups could lie in the higher overcrowding of the piperidino group, resulting in a higher leaving ability in the elimination step, after protonation by AcOH.

Following the analysis of table 2, it can also be pointed out, from the comparison between the yields of formation of TTF derivatives (determined by ^{1}H-NMR analysis of the reaction mixture) and the yields of the isolated pure TTF derivatives, that the work-up of the reaction with an average yield of recovery of about 80% can be considered as satisfactory for preparative purpose. At this stage, it must be emphasized that the analyses of the reaction mixtures before work-up, performed by ^{1}H-NMR spectroscopy or GC/MS analysis,

confirm the full selectivity of the "phosphonate way" in the synthesis of unsymmetrical TTF derivatives (any one of both potential symmetrical TTF derivatives could never be detected).

Lastly, it is noteworthy that the analysis of the reaction mixtures, before work-up, corroborate further the mechanism previously proposed for the formation of TTF derivatives:[14] the various by-products then formulated **5**, **24** – **26**, are always found in the mixtures; further, the O,O-diethyl phosphate is formed as expected in a molecular ratio nearly 1/1 to the TTF derivative.



5 **24** **25** **26**

Conclusion: The present results demonstrate that the synthesis of substituted TTF *via* "the phosphonate way" can be successfully applied:

-to phosphonates, with the dithiole ring disubstituted by alkyl, aryl or heteroatomic groups.

-to iminium salts, with the dithiole ring either unsubstituted, or mono- or disubstituted by alkyl or heteroatomic groups.

Further, our procedure affords a significant improvement in the overall yield of the TTF derivatives, by comparison with the results described in the literature.

The detailed study of the formation of the intermediate adducts and their transformation into TTF derivatives has also shown that the first step of the reaction occurs in high yields, often in a quantitative way. But the yields of the second step can strongly vary depending on the structure of the iminium salts: in particular, the piperidino group seems to be more suitable than the dimethyl amino group.

Lastly, the analysis of the various by-products in the reaction mixtures corroborates fully the previously proposed mechanism of the synthesis of unsymmetrically substituted TTF *via* the "phosphonate way".

Experimental

All reactions were performed under dry nitrogen; solvents were dried according to standard methods. - Melting point (uncorrected) were determined on hot microscope LEITZ . – IR: spectra were obtained on a PERKIN-ELMER (Series 377) spectrophotometer. - ^{1}H-NMR: spectra were recorded on a BRUKER Ac 250 (250 MHZ) or Ac 200 (200MHZ) spectrophotometer and ^{13}C-NMRspectra on a: BRUKER AC 200 (50.3 MHZ) spectrophotometer; $CDCl_3$ had being used as solvent. Chemical shifts are given in ppm (δ values) downfield relative to TMS. - ^{31}P-NMR spectra were recorded on a : BRUKER 200 (81 MHZ), spectrophotometer: Chemical shifts are given in ppm (δ values) downfield relative to H_3PO_4 . The mass spectra were recorded on a HEWLETT-PACKARD spectrometer (Series 5972A) coupled with a GC (model
5890) equiped with a OV1 column (25 m x 0.25 mm), or on a Jeol JMS-DX300 spectrometer[F.A.B. POS (matrice NBA ou GT), or E.I. (70 eV)] SPECTROMETER.

The separations and purifications of each compounds have been carried out by column chromatography: Silicagel, Si (60 -200 mesh E. Merck, Darmstadt, Germany).

Synthesis of TTF derivatives . - General Procedure. A solution of phosphonate (1 eq, 8 10^{-3} mol.) in dry THF (30 mL) was cooled to -78°C under magnetic stirring. A THF solution (5 mL) of potassium *tert*-butoxide (1.2 eq., 9.6 10^{-3} mol; 1. 07 g) was then added dropwise and allowed to react for 10 min. The iminium salt (1 eq., 8 10^{-3} mol.) was added in one portion to the reaction mixture maintained at -78°C under stirring. The mixture was allowed to reach to room temperature . Subsequently, anhydrous distilled glacial AcOH (10 eq , 1 mol) was added. The mixture was stirred at room temperature for additionnal T = 90min (except for compound **12**: T = 15 h). Then the solvent and the excess of AcOH were removed in vacuum. CH_2Cl_2 (about 35 mL) was added and the precipitate of KPF_6 obtained was filtered off; and the filtrate was concentrated and the residue submitted to column chromatography.

***Dimethyltetrathiafulvalene* 6**
Starting materials: phosphonate **17**[11] (8 10^{-3} mol; 2. 14 g) , and iminium salt **19**[11] (8 10^{-3} mol; 2. 64 g); chromatography SiO_2 / CH_2Cl_2.
TTF **6** characterization: brown orange powder. Mp 119°C. Yield 58% - ^{1}H-NMR ($CDCl_3$) δ = 1. 94 (s, CH_3), 6. 29 (s.CH). EI[M]$^+$: 234

***Trimethyltetrathiafulvalene* 7**
Starting materials : phosphonate **17**[11] (8 10^{-3} mol; 2. 14 g) , and iminium salt **20**[11] (8 10^{-3} mol; 2. 76 g); chromatography SiO_2 / toluene.
TTF **7** characterization: orange powder. Mp. 125°C. Yield 61% - ^{1}H-NMR ($CDCl_3$) δ = 1. 92 (s, 6H, CH_3), 2. 05 (s, 3H, CH_3), 5. 88 (s, CH) - EI[M]$^+$: 246

***Ethylenedithio dimethyltetrathiafulvalene* 8**
Starting materials: phosphonate **17**[11] (8 10^{-3} mol; 2. 14 g) , and iminium salt **21**[24, 25] (8 10^{-3} mol; 3. 05 g); chromatography: SiO_2 / toluene.
TTF **8** characterization: orange powder - Mp 169-171°C. Yield 23% - ^{1}H-NMR ($CDCl_3$) δ = 1. 93 (s, CH_3), 3. 27 (s, S-CH_2) - EI[M]$^+$: 322

Ethyleneoxythio dimethyltetrathiafulvalene **9**
Starting materials: phosphonate **17**[11] (8 10^{-3} mol; 2. 14 g) , and iminium salt **22**[26] (8 10^{-3} mol; 2. 79 g); chromatography SiO_2 / toluene.
TTF **9** characterization: orange powder. Mp 188-190°C -Yield 40% - ^{1}H-NMR ($CDCl_3$) δ = 1. 94 (s, 6H), 3. 12 (t, $^3J_{HH}$=4,53 Hz, 2H), 4. 44 (t, $^3J_{HH}$=4. 53 Hz, 2H) - EI[M]$^+$: 306, 174 (100%)

***Synthesis of the benzotetrathiafulvalene* 10**
Starting materials: phosphonate **1**[26] (8 10^{-3} mol; 2. 32 g), and iminium salt **19**[22](8 10^{-3} mol; 2. 64 g); chromatography: SiO_2 / CH_2Cl_2 / Hexane (1:1).
TTF **10** characterization: orange powder Mp 138-140°C - Yield 79% - ^{1}H-NMR ($CDCl_3$): δ = 6. 37 (s, CH), 7. 06-7. 26 (m, CH aromatics) - ^{13}C-RMN ($CDCl_3$); δ = 106. 62 (s, ^{5}C), 114. 50 (s, ^{4}C), 118. 79 (s, ^{6}C) 121. 74 (s, ^{2}CH) 125. 73 (s, ^{1}CH), 136. 68 (s,^{3}C) - EI[M]$^+$: 254.

***Synthesis of the methyl benzotetrathiafulvalene* 11**
Starting materials: phosphonate **1**[26](8 10^{-3} mol; 2. 32 g), and iminium salt **20**[22] (8 10^{-3} mol; 2. 76 g); chromatography SiO_2 / toluene
TTF **11** characterization: orange powder. Mp 196°C - Yield 68% - ^{1}H-NMR ($CDCl_3$): δ = 2. 08 (d, $^3J_{HH}$=1. 28 Hz, 3H), 5. 87(d, $^3J_{HH}$=1. 28 Hz, 3H) 7. 07-7. 26 (m, 4H) -^{13}C-RMN ($CDCl_3$); δ = 10. 39 (s, $^7CH_3$), 100.
08 (s, ^{5}C), 106. 58 (s, ^{8}CH), 115. 73 (s, ^{2}CH), 119. 70 (s, ^{1}CH), 125. 44 (s,^{6}C), 130. 99 (s, ^{3}C) - EI[M]$^+$: 268; Anal. Calc for C_{11} H_8 S_4 C,49.25; H, 4.10. Found: C, 49.32; H 4.07.

***Dimethyl benzotetrathiafulvalene* 4**
Starting materials: phosphonate **1**[26] (8 10^{-3} mol; 2. 32 g), and iminium salt **2**[22] (8 10^{-3} mol; 2. 87 g); chromatography: SiO_2 / toluene.

TTF 4 characterization: orange powder. Mp 220°C - Yield 80% - ^{1}H-NMR ($CDCl_3$): δ = 1. 96 (s, 6H), 7. 07-7. 26 (m, 4H) - ^{13}C-RMN ($CDCl_3$); δ =13. 62 (s, $^7CH_3$), 121. 68 (s, ^2CH), 122. 56 (s, ^5C), 125. 59 (s, ^1CH), 130. 74 (s, ^6C), 137. 10 (s,^3CH) - EI[M]$^+$: 284.

***Ethylenedithio benzotetrathiafulvalene* 12**

Starting materials: phosphonate **1**[26] (8 10^{-3} mol; 2. 32 g), and iminium salt **21**[24, 25] (8 10^{-3} mol; 3. 05 mg); After the removing in vacuo of the solvent and of the excess of AcOH, CH_2Cl_2 was added and the precipitate obtained was filtered off and treated by the sohxlet technic, the extractant being a mixture of water and CH_2Cl_2. The organic layer was evaporated and the recrystallisation of the residue from benzene afforded TTF **12**.

TTF **12** characterization: yellow crystals. Mp 225-228°C. Yield 40% - ^{1}H-NMR (acétone/CS_2): δ = (s, 3. 26, 3H), 7. 07-7. 26 (m, 4H) - EI[M]$^+$: 344, 152 (100%).

***Ethyleneoxythio benzotetrathiafulvalene* 13**

Starting materials: phosphonate **1**[26](8 10^{-3} mol; 2. 32 g) , and iminium salt **22**[26] (8 10^{-3} mol; 2. 79 g); chromatography: SiO_2 / toluene.

TTF **13** characterization: orange crystals. Mp 185°C - Yield 38% - ^{1}H-NMR ($CDCl_3$) δ = 3. 15 (t, $^3J_{HH}$=4. 00 Hz, S-CH_2), 4. 46 (t, $^3J_{HH}$=4. 49 Hz, O-CH_2), 7. 08-7. 26 (m, CH) - EI[M]$^+$: 328, 196 (100%)

***Ethylenedithio tetrathiafulvalene* 14**

Starting materials: phosphonate **18**[27, 28] (8 10^{-3} mol; 2. 64 g) and iminium salt **19**[22] (8 10^{-3} mol; 2. 64 g); chromatography: SiO_2 / toluene.

TTF **14** characterization: brown orange powder. Mp 208-211°C - Yield 50% - ^{1}H-NMR ($CDCl_3$) δ = 3. 29 (s, CH_2), 6. 33 (s, CH), - EI[M]$^+$: 294, 146 (100%)

***Ethylenedithio methyltetrathiafulvalene* 15**

Starting materials: phosphonate **18**[27, 28] (8 10^{-3} mol; 2. 64 g) , and iminium salt **20**[22] (8 10^{-3} mol; 2. 76 g); chromatography: SiO_2 / toluene.

TTF **15** characterization: brown orange powder - Mp 134-136°C - Yield 58% ^{1}H-NMR ($CDCl_3$) δ = 2. 07 (d, $^4J_{HH}$= 1. 40 Hz, CH_3), 3. 29 (s,CH_2), 5. 87 (d, $^4J_{HH}$= 1. 40 Hz, CH) - EI[M]$^+$: 308, 116 (100%)

***Ethylenedithiodimethyltetrathiafulvalene* 8'**

Starting materials: phosphonate **18**[27, 28] (8 10^{-3} mol; 2. 64 g), and iminium salt **2**[22] (8 10^{-3} mol; 2. 87 g); chromatography: SiO_2 / toluene.

TTF **8'** characterization: brown orange powder. Mp 169-171°C -Yield 82% - ^{1}H-NMR ($CDCl_3$) δ = 1. 93 (s, CH_3), 3. 27 (s.CH_2) - EI[M]$^+$: 322

***Ethyleneoxythio tetrathiafulvalene* 16**

Starting materials: phosphonate **18**[27, 28] (8 10^{-3} mol; 2. 64 g) , and iminium salt **22**[24] (8 10^{-3} mol; 2. 79 g mg); T = 90 min.; chromatography: SiO_2 / toluene.

TTF **16** characterization: brown orange powder. Mp 195°C - Yield 1^{12}4% - ^{1}H-NMR ($CDCl_3$) δ = 3. 29 (s, S-CH_2), 6. 33 (s.O-CH_2) - EI[M]$^+$: 368, 88 (100%)

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