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A Convenient One-Step Synthesis of Formyltetrathiafulvalene Vinylogs : Building Blocks for New NLO Materials

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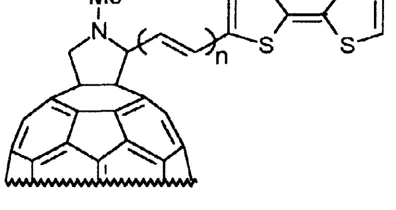
Abstract: A new method for the synthesis of formyltetrathiafulvalene vinylogs in which tetrathiafulvalene (TTF) or a substituted derivative of TTF is metalated with lithium diisopropylamide and then reacted with a vinylogous amide to yield the corresponding short polyenals in a one-pot process is described. © 1998 Elsevier Science Ltd. All rights reserved.

Lithiation of tetratiafulvalenes constitutes the most significant route for the preparation of TTF derivatives provided that the metalated species formed give rise to a wealth of new derivatives.[1,2] Moreover, several derivatives thus obtained bear functional groups (carboxaldehyde, ester, carboxylic acid, hydroxymethyl, amine) which can be further reacted to afford more complex molecules which have made of TTF one of the most important electroactive molecules to be used as building blocks in supramolecular chemistry[3] and molecular electronics.[4]

During the last years we have been concerned with the study of organic molecules bearing electron donor and electron acceptor units because of their potential applications in optical and electronic devices.[5] We have recently reported on the synthesis and study of electrooptical properties of intramolecular donor-acceptor (D-A) dyads (**1**, **2**) containing TTF units in which both donor and acceptor moieties are connected by different spacers (Figure).[6] During the course of these investigations the known TTF derivatives **4a** and **5a** (Scheme) as well as other new diferently substituted vinilogs of **5** were needed as starting materials provided that the length of the conjugated spacer has proved to be a most important factor for the preparation of D-A dyads exhibiting nonlinear optical (NLO) properties.[7]



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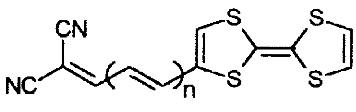

2

Figure

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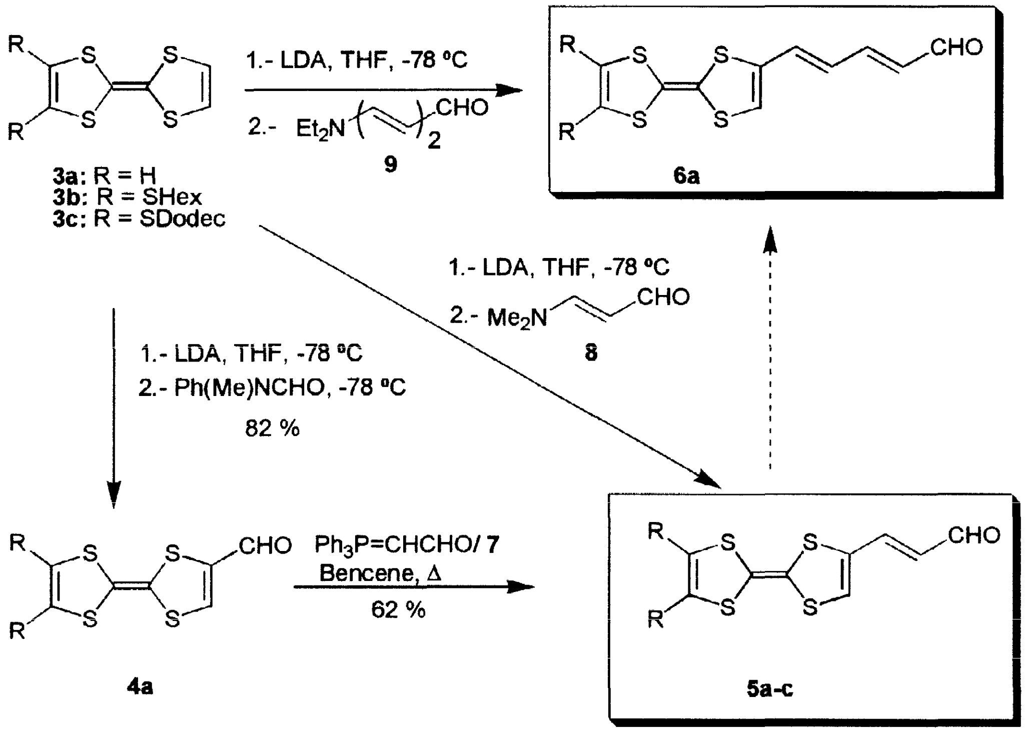
The synthesis of formyl-TTF (**4a**) was first reported by Green[1] by reaction of monolithio-TTF with dimethylformamide. Afterwards Garín, Bryce and co-workers investigated thoroughly this reaction with a variety of formylating reagents in order to increase the yields and optimize the preparation of formyl-TTF (**4a**).[8] Subsequent Wittig reaction of formyl-TTF (**4a**) with phosphorane **7** leads to the formyl-TTF vinylog **5a** with an overall yield of 51 % starting from TTF (Scheme). To the best of our knowledge the preparation of higher vinylogs than **5a** by following this or any other synthetic route has not yet been reported.

In this work we describe an alternative one-pot synthesis of **5a-c** as well as the synthesis of the higher vinylog **6a**. The key step in the general reaction scheme involves the reaction of monolithio-TTFs (generated from TTF and lithium diisopropylamide)[1] with the commercially available *N,N*-dimethylaminoacrolein (**8**) to yield **5a-c** and with 5-(*N,N*-diethylamino)-4-pentadienal[9] (**9**) to obtain **6a** by following Jutz's procedure[10] which has been recently extended to several organolithium systems by Friedli, Yang and Marder.[11] Novel tetrathiafulvalenes **3b** and **3c** were obtained as a red oil and a red solid respectively by using the usual multistep procedure which involves first trimethyl phosphite-mediated cross-coupling reaction[12] of the corresponding 4,5-bis(dialkylthio)-1,3-dithiole-2-thiones[13] and 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-one[14] followed by demethoxycarbonylation reaction[15] of the TTF derivative thus formed by treatment with lithium bromide in HMPA.



Scheme

In a typical experiment for the preparation of vinylogs **5a-c** and **6**, 1 equivalent of the vinylogous amide (**8** or **9**) was added to a lithiated TTF solution in THF, prepared earlier from TTF (1 equiv.) and lithium diisopropylamide (1.5 equiv.) at -78 °C. The reaction mixture was stirred at -78 °C for an hour and then slowly warmed to room temperature over twelve hours. The solution was acidified with 2N HCl, the organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined extracts were washed with water, dried with magnesium sulfate and evaporated in vacuum. The residue thus obtained was purified by flash chromatography.[16]

When the reaction is carried out with the commercially available *N,N*-(dimethylamino)acrolein (**8**) yields of 60, 52 and 50 % were obtained for the unsubstituted, 4,5-dihexhylthio and 4,5-didodecylthio-tetrathiafulvalene respectively, thus competing favorably with the yields obtained by using the two-step procedure previously described. On the other hand, the use of 5-(*N,N*-diethylamino)-4-pentadienal (**9**) as the electrophilic reagent affords 5-(tetrathiafulvalenyl)penta-2,4-dien-1-al (**6a**) in a 32 % yield. All-*trans* vinylog amides were used in all cases as starting materials and only all-*trans* formyl-TTF vinylogs were obtained according to the coupling constants observed in the ^{1}H-NMR spectra.[16]

The aldehyde group of **6a** was easily converted into a strong acceptor group by condensation with malononitrile to form **2** (n = 2).[16] The molecular hyperpolarizability of compound **2** (n = 2) was measured in $CHCl_3$ using the EFISH technique at 1907 nm. The value obtained ($\mu\beta$ = 630. 10^{-48} esu, $\mu\beta_0$ = 320. 10^{-48} esu) agrees with the calculated one ($\mu\beta_0$ = 265. 10^{-48} esu at the FF-PM3 level) and is significantly higher than that obtained for **2** (n = 1)[17], thus opening up the way to other acceptor moieties with interesting intramolecular charge-transfer (ICT) properties. Interestingly, although a slight bathochromic shift of the ICT band is observed on going from **5a** to **6a** (515 nd 526 nm, respectively, in $CHCl_3$), a rather unusual hypsochromic shift is observed in compounds **2** when the extended system is increased[17] (n = 0, 624 nm ; n = 1 , 618 nm ; n = 2, 608 nm ; in CH_2Cl_2 and 639, 636 and 628 nm, respectively, in $CHCl_3$).

In summary, we have developed a facile one-pot synthesis of formyl-TTF vinylogs (**5a-c**, **6a**) in satisfactory yields. Starting materials are either commercially available or easily synthesized by using literature procedures. Furthermore, the fact that the syntheses of even higher vinylogous amides are reported in the literature[9] widens the scope of the reaction towards longer polyenals. The aldehydes thus obtained may be condensed with a variety of acceptor molecules in order to obtain donor-acceptor polyenes containing TTF units. Work is in progress in order to obtain different TTF containing D-A systems, the measurements of the first hyperpolarizabilities (β) of some of these materials being currently under investigation.

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16. Analytical and spectroscopic data of **5a** are in full agreement with the previously reported for the same compound prepared by the two step procedure.[8] Selected spectroscopic data for :
    5b : M.p. (°C) : 75 . IR (KBr) : ν = 2960, 2930, 2860, 1680, 1610, 1520, 1465, 1130 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$) : δ = 9.58 (d, *J*=7.4, 1H), 7.17 (d, *J*=15.4, 1H), 6.87 (s, 1H), 5.96 (dd, *J*=15.4, 7.4, 1H), 2.82 (m, 4H), 1.62 (m, 4H), 1.41 (m, 4H), 1.28 (m, 8H), 0.9 (t, 6H). ^{13}C-NMR (75 MHz, CDCl$_3$) 192.2, 140.4, 134.3, 129.8, 129.6, 129.4, 127.5, 112.2, 110.1, 36.3, 31.3, 29.7, 28.2, 22.5, 14.0. **5c** : M.p. (°C) : 88. IR (KBr) : ν = 2960, 2920, 1850, 1685, 1670, 1610, 1520, 1460, 1130 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$) : δ = 9.57 (d, *J*=7.7 Hz, 1H), 7.16 (d, *J*=15.4 Hz, 1H), 6.87 (s, 1H), 5.95 (dd, *J*=15.4, 7.4 Hz, 1H), 2.81 (m, 4H), 1.60 (m, 4H), 1.42 (m, 4H), 1.26 (s, 32 H), 0.88 (t, 6H). ^{13}C-NMR (75 MHz, CDCl$_3$) 192.3, 140.5, 134.2, 129.8, 129.6, 128.4, 127.5, 111.7, 110.1, 36.3, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 28.5, 22.7, 14.1 . **6a** : M.p. (°C) : 158. IR (KBr) : ν = 1660, 1605, 1582, 1504, 1142, 1160 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$) : δ = 9.59 (d, *J*=7.8 Hz, 1H), 7.12 (dd, *J* = 15.3, 11.4 Hz, 1H), 6.75 (d, *J*= 15.3 Hz, 1H), 6.61 (s, 1H), 6.35 (s, 2H), 6.27 (dd, *J* = 14.7, 11.4 Hz, 1H), 6.22 (dd, *J* = 14.7, 7.8 Hz, 1H). ^{13}C-NMR (75 MHz, CDCl$_3$) 193.1, 150.4, 135.2, 132.3, 131.9, 128.7, 125.1, 119.1, 118.9, 114.1, 106.1. **2** (n = 2) : M.p. (°C) : 201. IR (KBr) : ν = 2230, 2219, 1584, 1538, 1496, 1363, 1287, 1153 cm^{-1}. ^{1}H-NMR (300 MHz, DMSO) : δ = 8.14 (d, *J*=11.2 Hz, 1H), 7.29 (s, 1H), 7.24 (dd, *J* = 13.68, 12.7 Hz, 1H), 7.08 (d, *J*= 13.68 Hz, 1H),), 6.93 (dd, *J* = 12.7, 12.7 Hz, 1H) 6.75 (s, 2H) 6.51 (dd, *J* = 12.7, 11.2 Hz, 1H).
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