A Photochemical Synthesis of Bis(ethylenedithiolo)tetrathiafulvalene

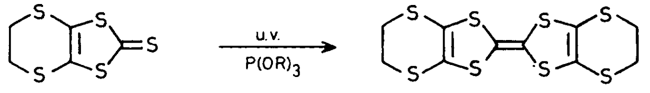
Miloslav Šorm, Stanislav Nešpůrek, Olen Ryba, and Vladimír Kubánek

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

Bis(ethylenedithiolo)tetrathiafulvalene was prepared by a photochemical desulphurization of 4,5-ethylenedithiolo-1,3-dithiole-2-thione (**1**), and the effect of the type of solvent, nucleophilic agent and its concentration, and temperature on the yield of the reaction is discussed.

There is a great interest in organic superconducting materials because of the theoretical possibility of preparing room-temperature superconductors. Recently, superconductivity has been found in radical salts of bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF).[1]

Tetrathiafulvalene and its derivatives can be prepared by various procedures,[2] but the procedure particularly suitable for the preparation of TTF derivatives containing electron-withdrawing groups[3] is a one-step thermal desulphurization of 2-thioxo-1,3-dithioles with trivalent phosphorous com-



(1) BEDT-TTF

Scheme 1

pounds.[4] In the presence of electron-donating groups the reaction proceeds with much greater difficulty, or by a different mechanism with formation of a complicated mixture of products.

A direct desulphurization of 4,5-ethylenedithiolo-1,3-dithiole-2-thione (**1**), by treating it with triethyl phosphite at 105—115 °C in a low yield was described by Mizuno *et al.*[5] Moses *et al.*[6] using the same procedure were unsuccessful in their attempts to prepare BEDT-TTF. We have also been unable to prepare BEDT-TTF using the same method or various modifications (*e.g.* temperature, time, type of agent). We have always obtained a complicated mixture of products.

The reactivity of PR_3 agents in the desulphurization of various compounds may be enhanced by u.v. radiation.[7] The first photochemical preparation of TTF derivatives containing electron-donating groups has been described by Ueno *et al.*[8] in the presence of hexabutyldistannate. Quite recently, Tsujimoto *et al.*[9] have prepared tetraphenyltetrathiafulvalene by photochemical desulphurization of the corresponding 2-thioxo-1,3-dithiole in the presence of triethylphosphite and triethylamine in acetonitrile.

In this communication we describe the preparation of BEDT-TTF by employing a photochemical procedure in the reaction of (**1**) with trivalent phosphorus compounds (Scheme 1) under various experimental conditions. The results are summarized in Table 1.

The reaction of (**1**) with triethyl phosphite was carried out in solvents with various donor properties. The reaction proceeds best in benzene; in the other cases the reaction yields were much lower, or the reaction did not take place at all. The solvent has a decisive effect on the photochemical reaction of $P(OEt)_3$ with (**1**). The type of agents used also considerably affects the course of the reaction. In Table 1, trivalent phosphorus compounds have been arranged in order of decreasing electron-donating activity (NEt_3 is given for the sake of illustration). It can be seen that any significant reaction proceeds only with triethyl phosphite, and with trimethyl phosphite to a small extent. No formation of BEDT-TTF could be observed in the other cases, including in the presence of triethylamine. Similarly, desulphurization agents possessing pronounced electron-donating or electron-withdrawing properties block the photochemical reaction. Table 1 also shows the effect of increase of concentration of triethyl phosphite (chosen as a representative agent) on reaction yields. The yields of BEDT-TTF increase with increasing concentration of the agent up to a certain value, then decrease again. The best results were obtained at a molar excess of $P(OEt)_3$ from 7 to 15 times with respect to (**1**). Elevated temperature (105—115 °C) has an unfavourable effect on the photochemical course of the reaction, decreasing the yield in the reaction using $P(OEt)_3$ as solvent. The amount of the agent used affects not only the yield, but also the rate of formation of BEDT-TTF. The higher the concentration of the agent, the higher the reaction rate. For instance, at a two-molar excess the product separated from the reaction mixture only after several hours; if the reaction was carried out in the agent alone, the product separated immediately upon irradiation. The photochemical reaction is very sensitive to the reaction conditions because of the formation of side products which stop the further course of the reaction.

Table 1. Photolysis of (**1**) under various conditions.[a]

Solvent	Yield[b], %	Agent[c]	Yield[d], %	$P(OEt)_3$, mol/mol (**1**)	Yield[d], %
Ethanol	0	PPh_3	0	2	5
Tetrahydrofuran	7	$P(OEt)_3$	58	4	47
Toluene	29	$P(OMe)_3$	8	7	58
Benzene	58	PCl_3	0	15	57
Acetonitrile	0	NEt_3	0	R[e]	23
$P(OEt)_3$	23			R[f]	18

[a] $T = 55 \pm 3$ °C, high-pressure mercury discharge tube HBO-200 with filter transmitting light of wavelength longer than 280 nm. [b] Agent $P(OEt)_3$ [7 mol/mol (**1**)]. [c] No BEDT-TTF formed in the absence of agent. [d] Benzene as solvent. [e] Solvent $P(OEt)_3$. [f] 0.2 g of (**1**), 1 ml $P(OEt)_3$, simax cell, 105—115 °C, irradiated 1 h.

From our results we found that the following procedure was optimal for the synthesis of BEDT-TTF: 1.8 g of (**1**), 45 ml benzene, and 9 ml $P(OEt)_3$ were dissolved in a quartz cell at 55 ± 3 °C, and the solution was purged with nitrogen (15 min). The yellow solution was irradiated by light of wavelength $\lambda > 280$ nm, from a high-pressure discharge tube HBO-200 (GDR) with a filter, at the same temperature. The distance between the discharge tube and the cell was 0.2 m. Within 15 min, a brick-red product began to separate from the solution. After 8 h the irradiation was terminated, the product was filtered off, washed with benzene and diethyl ether, dried, and crystallized from chlorobenzene under nitrogen. BEDT-TTF crystals were obtained in 58% yield (0.9 g), m.p. 258—260 °C (decomp.) [ref.[5] m.p. >250 °C (decomposition)]. The results of elemental analysis and spectral data were in agreement with the BEDT-TTF structure. The filtrate contained unreacted (**1**), triethylthiophosphite, and a number of brown-red side products (as determined by chromatography on a thin silica gel layer).

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