

Useful Wittig Reagents in 1,3-Dithiole and Tetrathiafulvalene (TTF) Chemistry: 2-Thioxo- and 2-Oxo-1,3-dithiol-4-ylmethyl(triphenyl)phosphonium Bromides

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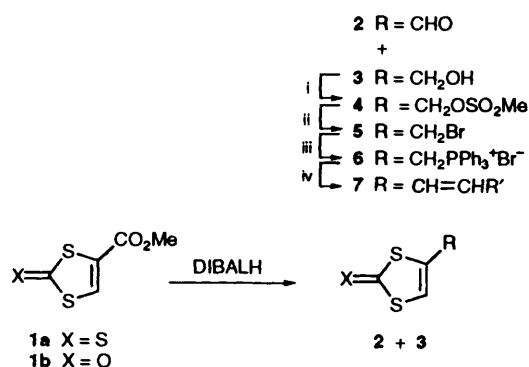
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DIBALH reduction of the methyl ester group of 2-(thi)oxo-1,3-dithioles **1a** and **1b** selectively affords the corresponding alcohols **3a** and **3b** which are readily converted into the title compounds **6a** and **6b** under standard conditions; the latter behave as useful Wittig reagents leading to sulfur-rich and space-extended TTF derivatives.

The synthesis¹ of TTF derivatives continues in order to improve the electrical properties of their charge-transfer salts.² Most efforts consist of designing new π -donors which may favour the growing of organic metals endowed with high dimensionality,³ in order to avoid a breakdown of the electroconductibility possible with monodimensional materials. Of the trends in this field, several S-rich and extended π -donor analogues of TTF have been synthesized, notably *via* Wittig (Horner) P-reagents bearing the 1,3-dithiol-2-ylidene moiety.⁴ In order to extend the flexibility of this strategy, we have focused on the still unknown title compounds **6a** and **6b**, taking into account the prominent role of 2-(thi)oxo-1,3-dithioles in TTF chemistry.¹ We report here a route providing ready access to these new reagents and describe some preliminary results emphasizing their ability to undergo Wittig reactions, particularly with (poly)formyl-TTFs.[†]

Our synthetic approach involves the classical steps outlined in Scheme 1. First, the reduction of an ester function on a 1,3-



Scheme 1 Reagents and conditions: i, MeSO_2Cl , Et_3N , CH_2Cl_2 , -10°C , 25 min; ii, Bu_4NBr , CH_2Cl_2 , room temp., 1.5 h; iii, PPh_3 (2 equiv.), toluene, reflux, 5 h; iv, Et_3N (excess), $\text{R}'\text{CHO}$, CHCl_3 , room temp., 1.5–3 h with **6a** or DMF, room temp., 24 h with **6b**.

dithiole ring was, according to previous reports, a challenging problem.⁵ However, by using DIBALH (CH_2Cl_2 solution) we could obtain either the aldehydes **2a**, **b** or the alcohols **3a**, **b**, the selectivity of this reaction mainly depending on the temperature.⁶ Thus, when performed at -85°C for 1 h, the

reduction of **1a** (DIBALH/ester: 1.5 in molar ratio) affords a mixture of **2a** (67%) and **3a** (21%) after SiO_2 column chromatography (eluent: CH_2Cl_2), whereas under similar temperature conditions the reduction of **1b** appears to be more difficult (3.5 h) and gives rise to **2b** and **3b** in lower yields (45 and 14% respectively) along with 20% of recovered **1b**. On the other hand, when carried out through a slow raising of the temperature from -85 to -20°C over a period of 4.2 h (DIBALH/ester: 2.3 in molar ratio) this reduction leads almost exclusively to the corresponding alcohols **3a** (86% isolated yield) and **3b** (54%), the lower yield in this latter case being mainly due to losses during the work-up given the solubility of **3b** in water.

Both alcohols **3a** and **3b** are readily converted into the phosphonium bromides **6a** and **6b** (overall yields > 75%) *via* their corresponding crude mesylates **4a**, **b**[‡] and bromides **5a**, **b**,⁷ formed under standard conditions,⁸ followed by treatment of the latter with triphenylphosphine.

In order to test the scope of these new phosphonium salts in TTF chemistry, the Wittig reactions of **6a** have been studied with the aldehydes **2a**, formyl-TTF⁹ and each of the *Z*- and *E*-isomers of tetraformyl-TTF-bis(diethyl acetal)¹⁰ in the presence of triethylamine as the base (CHCl_3 or CH_2Cl_2 solvent). The expected olefination products are obtained with fair to excellent yields, respectively **7a** (60%), **8a** (83%), **9a** (95%) and **10a** (95%); similarly, **8b** is produced in a lower yield (65%) from **6b**. As observed in the Wittig reactions of $\text{Ph}_3\text{PCH}_2\text{PhBr}$ with aldehydes,¹¹ **7a** and **8a** are obtained as a mixture of *cis* and *trans* diastereoisomers, which are gradually converted in CHCl_3 solution into the less soluble *trans*-derivative, this latter being isolated in the pure state in the case of **8a** [red-brown powder, m.p. 210°C (decomp.); $\delta_{\text{H}}([\text{}^2\text{H}_6]\text{DMSO})$ 6.51 (1 H, d), 6.76 (1 H, d, *J* 16 Hz), 6.75 (3 H, s), 7.09 (1 H, s) and 7.66 (1 H, s)]. In the same way, the bis-olefination compounds **9a** and **10a** consist of three *cis-cis*, *trans-cis* and *trans-trans* isomers, ¹H NMR analysis of which show the *trans-trans* derivative to be formed as the less abundant in the mixture. In addition to the usual characterization data, it should also be noted that the cyclovoltammogram of **8a** (pure *trans*-isomer) exhibits, as expected, two reversible $1 e^-$ oxidation peaks, at 0.67 and 0.96 V/SCE (SCE = standard calomel electrode) at 20°C [THF , Bu_4NClO_4 (0.1 mol dm^{-3})]; these values reveal a slight electron-withdrawing effect of the sulfur-rich substituent on the TTF nucleus, by comparison with the lower values (0.53 and 0.78 V) for TTF itself in the same conditions.

In conclusion, these preliminary results show that **6a** and **6b** are useful synthetic intermediates in TTF chemistry, and their Wittig olefination products constitute promising precursors of new TTFs by dimerization–desulfurization (or deoxygenation) of their 1,3-dithiole-(thi)one functionality.

[†] This work was presented, in part, as an oral communication at the International Conference on Science and Technology of Synthetic Metals, ICSM '92, Göteborg, Sweden, August 12–18, 1992.

[‡] Because of their high sensitivity, compounds **4a** and **4b** should be handled as dilute solutions (CH_2Cl_2) and not in the pure state.

