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

Tomasz Nozdryn,^a Jack Cousseau,^{*,a} Alain Gorgues,^{*,a} Michel Jubault,^a Jesus Orduna,^b Santiago Uriel^b and Javier Garin^b

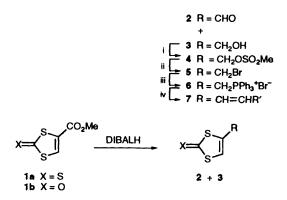
^a Laboratoire de Chimie Organique Fondamentale et Appliquée, Université d'Angers, 2 Bd Lavoisier, 49045 Angers Cedex, France

^b Laboratorio de Química Organica, ICMA, CSIC, Universidad de Zaragoza, 50009 Zaragoza, Spain

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." 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, PPh₃ (2 equiv.), toluene, reflux, 5 h; iv, Et_3N (excess), R'CHO, CHCl₃, 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 (CH₂Cl₂ 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 SiO₂ column chromatography (eluent: CH₂Cl₂), 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.

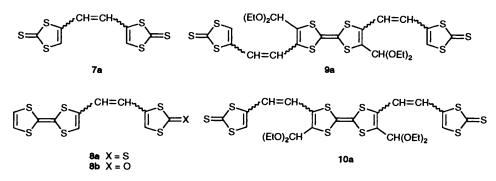
Both alcohols **3a** and **3b** are readily converted into the phosphonium bromides **6a** and **6b** (overall yields > 75%) via their corresponding crude mesylates **4a**, **b** \ddagger and bromides **5a**, **b**, ⁷ formed under standard conditions,⁸ followed by treatment of the latter with triphenylphosphine.

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 (CHCl₃ or CH₂Cl₂ 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 Ph₃PCH₂PhBr with aldehydes,¹¹ 7a and 8a are obtained as a mixture of *cis* and trans diastereoisomers, which are gradually converted in CHCl₃ 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.); $\delta_{\rm H}([^{2}{\rm H}_{6}]{\rm DMSO})$ 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, Bu₄N ClO_4 (0.1 mol dm⁻³)]; these values reveal a slight electronwithdrawing 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.

 $[\]ddagger$ Because of their high sensitivity, compounds 4a and 4b should be handled as dilute solutions (CH₂Cl₂) and not in the pure state.



Experimental

Reduction of the Esters 1.—DIBALH (1 mol dm⁻³ in CH₂Cl₂; 4 mmol) was added dropwise over 30 min to a cooled (-85 °C) solution of the ester 1 (2.6 mmol) in CH₂Cl₂ (15 cm³), and the reaction mixture was stirred at -85 °C for 35 min in the case of 1a or 180 min in the case of 1b. The reaction was then quenched with 1 mol dm⁻³ aq. HCl, and the organic phase dried to give the aldehydes 2a or 2b as the major products (see the text above).

The alcohols 3 were formed as the main products by adding DIBALH (1 mol dm⁻³ in CH₂Cl₂; 6.5 mmol) at -85 °C to the ester 1, followed by a slow warming up with stirring, either to -25 °C in the case of 1a (220 min) or to -40 °C in the case of 1b (270 min); the reactions were quenched with 1 mol dm⁻³ aq. HCl and after work-up gave the alcohols 3a or 3b as indicated in the text.

4-Formyl-1,3-dithiol-e-2-thione **2a**. Bright yellow plates, m.p. 87 °C; $\delta_{\rm H}$ (CDCl₃) 8.01 (1 H, s) and 9.53 (1 H, s) [lit.,¹² m.p. 83 °C; $\delta_{\rm H}$ 7.97 (1 H, s) and 9.53 (1 H, s)].

4-Hydroxymethyl-1,3-dithiole-2-thione **3a**. Yellow powder, m.p. 43-44 °C; $\delta_{\rm H}$ (CDCl₃) 2.5 (1 H, br s), 4.6 (2 H, s) and 6.97 (1 H, s).

4-Formyl-1,3-dithiol-2-one **2b**. White needles, m.p. 78–79 °C; $\delta_{\rm H}$ (CDCl₃) 7.86 (1 H, s) and 9.54 (1 H, s).

4-Hydroxymethyl-1,3-dithiol-2-one **3b** colourless liquid; $\delta_{\rm H}$ -(CDCl₃) 2.5 (1 H, br s), 4.57 (2 H, s) and 6.73 (1 H, s).

Synthesis of the Phosphonium Salts 6.—To a cooled $(-10^{\circ}C)$ solution of the alcohol 3 (20 mmol) and triethylamine (30 mmol) in CH₂Cl₂ (90 cm³) was added methanesulfonyl chloride (30 mmol) dropwise over ca. 20 min., with continued stirring for 1 h at 0 °C. The reaction mixture was then washed with water and the organic phase dried (MgSO₄) and filtered, Bu₄NBr (40 mmol) was then added to it, and the solution stirred at room temperature for 2 h. The reaction mixture was then concentrated under reduced pressure at room temperature and the onium salts were eliminated by chromatography (Et₂O) through a short SiO₂ column (15 cm). After evaporation of solvents (CH₂Cl₂, Et₂O) under reduced pressure at room temperature, the crude bromo derivative 5 was dissolved in toluene (80 cm³) and PPh₃ (40 mmol) added to the solution which was then refluxed for 8 h. The final phosphonium salt 6 was filtered off.

2-Thioxo-1,3-dithiol-4-ylmethyl(triphenyl)phosphonium bromide **6a**. Yellow powder (8.12 g, 83%), m.p. ~ 264 °C (decomp.); $\delta_{\rm H}$ (CDCl₃) 6.4 (2 H, d, ³J_{PH} 14.3 Hz), 7.3 (1 H, s) and 7.5–8.3 (15 H, m).

2-*Oxo*-1,3-*dithiol*-4-ylmethyl(triphenyl)phosphonium bromide **6b**. White powder (5.68 g, 60%), m.p. ~264 °C (decomp.); $\delta_{H}([{}^{2}H_{6}]DMSO)$ 5.29 (2 H, d, ${}^{3}J_{PH}$ 14.8 Hz), 6.85 (1 H, d, ${}^{4}J_{PH}$ 4 Hz) and 7.5–7.85 (15 H, m).

Acknowledgements

We are indebted to DGICYT (Project PB 91-0932) and to the French and Spanish Governments (Integrated Action 277B and PICASSO 1993) for financial support, as well as to the Ministère des Affaires Etrangères (French Embassy in Poland) for a grant to T. N.

References

- 1 A. Krief, Tetrahedron, 1986, 42, 1209; G. Schukat, A. M. Richter and E. Fanghanel, Sulfur Reports, 1987, 7, 155.
- 2 S. Kagoshima, H. Nagasawa and T. Sambongi, One Dimensional Conductors, Springer Verlag, Berlin, 1987, pp. 1-105; G. Saito and S. Kagoshima, The Physics and Chemistry of Organic Superconductors, Springer Verlag, London, 1990, pp. 1-428.
- 3 M. R. Bryce and L. C. Murphy, *Nature*, 1984, **309**, 119; M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355.
- 4 See the following papers and references cited: M. R. Bryce and A. J. Moore, Synth. Metals, 1988, 27, B557; M. R. Bryce, A. J. Moore, D. Lorcy, A. S. Dhindsa and A. Robert, J. Chem. Soc., Chem. Commun., 1990, 470; M. Sallé, A. Belyasmine, A. Gorgues, M. Jubault and N. Soyer, Tetrahedron Lett., 1991, 32, 2897; A. S. Benhamed-Gasmi, P. Frère, B. Garrigues, M. Jubault, R. Carlier and F. Texier, Tetrahedron Lett., 1992, 33, 6457.
- 5 W. R. Hertler, J. Org. Chem., 1976, 41, 1412; C. U. Pittmann, M. Narita and Y. F. Liang, J. Org. Chem., 1976, 41, 2855; U. Jordis and M. Rudolf, Phosphorus and Sulfur, 1984, 19, 279; S.-H. Hsu and L. Y. Chiang, Synth. Met., 1988, 27, B651; M. Sallé, A. Gorgues, J. M. Fabre, K. Bechgaard, M. Jubault and F. Texier, J. Chem. Soc., Chem. Commun., 1989, 1520.
- 6 L. I. Zakharkhin and I. M. Khorlina, Tetrahedron Lett., 1962, 619; E. Winterfeldt, Synthesis, 1975, 617.
- 7 In a previous work (N. F. Haley and M. W. Fitchner, J. Org. Chem., 1980, 45, 175), compound 5a was reported to be very unstable; however, we observed no important degradation during its reaction with PPh₃, provided it was used in a dilute medium as soon as formed.
- 8 B. Ledoussal, A. Le Coq, A. Gorgues and A. Meyer, *Tetrahedron*, 1983, **39**, 2185.
- 9 D. C. Green, J. Org. Chem., 1979, 44, 1476; by using N-methyl-Nphenylformamide or N-formylmorpholine as formylating agent of TTFLi we improved the yield of formation of TTF-CHO (52-65%).
- 10 M. Sallé, A. Gorgues, M. Jubault, K. Boubekeur and P. Batail, *Tetrahedron*, 1992, 48, 3081.
- 11 I. Gosney, in Organophosphorus Reagents in Organic Synthesis, ed. J. I. G. Cadogan, Academic Press, London, 1979, p. 77.
- 12 G. Seitz and P. Imming, Arch. Pharm., 1988, 321, 757.

Paper 3/03380E Received 11th June 1993 Accepted 14th June 1993