JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 8
1983

Tetraformyltetrathiafulvalene(TFTTF): Synthesis and Some Uses as a Precursor of Polyfunctionalised Tetrathiafulvalenes†

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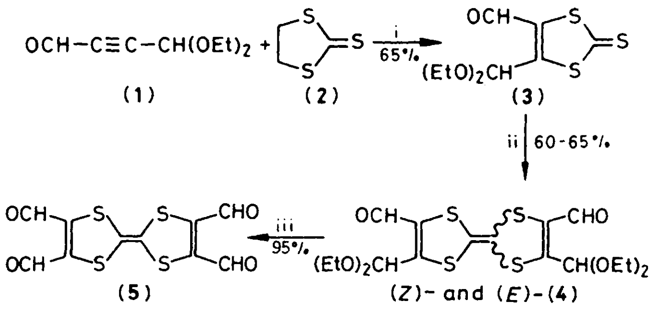
Tetraformyltetrathiafulvalene has been prepared in a short, efficient synthesis and a few preliminary results emphasise its use as a precursor of polyfunctionalised tetrathiafulvalenes; a tetravinyl derivative is readily obtained *via* a Wittig reaction and has been shown, by its complexation with tetracyanoquinodimethane, to be a good π-donor.

Tetrathiafulvalene (TTF) and its derivatives have been of great interest since it was discovered that, with suitable acceptors, they could form charge-transfer salts. These salts behave as 'organic metals' owing to their high conductivity.[1] Numerous subtle modifications of the electronic and topological properties of this donor have resulted in the synthesis of substituted TTF derivatives[2] and/or replacement of the S atoms with Se[1,2] and, more recently, with Te.[3] The discovery[4] of superconductivity in the electrogenerated $(TMTSF)_2X$ (TMTSF = tetramethyltetraselenafulvalene) family[4b] and the indication of related phenomena in the $(TMTTF)_2X$ (TMTTF = tetramethyltetrathiafulvalene) series[4c] suggest[4c–e] that further modifications of TTF might still be of interest.

We report here an efficient synthesis of the previously unknown tetraformyltetrathiafulvalene (TFTTF)[5] and some preliminary results illustrating the tremendous synthetic potential of this compound to yield polyfunctionalised TTF derivatives.



Scheme 1. i, Equimolar amounts of (**1**) and (**2**), reflux, 7 h, xylene, N_2; ii, 1.5 mol of (**3**), 1 mol of $Co_2(CO)_8$, toluene, N_2, 0.5 h at 40 °C, then 1.5 h under reflux; iii, HCO_2H, CH_2Cl_2, 10 min, room temp.

In our approach to the title compound (**5**) (Scheme 1) we preferred to use the readily prepared and easy-to-handle diethyl acetal (**1**),[6a] rather than the more electrophilic but unstable dialdehyde;[6b] the acetal afforded (**3**)‡§ isolated (65% yield) as yellow needles, m.p. 42—43 °C, after SiO_2 column chromatography (pentane–ether eluant) and recrystallization (light petroleum). Neither phosphines nor phosphites[1b] induced the required dimerisation with desulphurisation; this was neatly performed, however, using octacarbonyldicobalt.[7] After separation of a black pyrophoric insoluble material, the solution was filtered through a short SiO_2 column (CH_2Cl_2–Et_2O eluant) and essentially equal amounts of (*Z*)- and (*E*)-(**4**) were obtained and eventually separated by chromatography on a SiO_2 column (CH_2Cl_2–Et_2O,10:1):(*E*)-(**4**), purple crystals, m.p. 172 °C; i.r. ($CHCl_3$) 1655 cm^{-1}; ^1H n.m.r. (Me_4Si), 1.25 (t), 3.75 (q), 5.83 (s), and 10.05 (s); (*Z*)-(**4**), purple crystals, m.p. 130—132 °C; i.r. ($CHCl_3$) 1660 cm^{-1}; same ^1H n.m.r. spectrum. Quantitative precipitation of dark blue crystals of (**5**), m.p. 280 °C (decomp.), i.r. (Nujol) 1660 cm^{-1}, ^1H n.m.r. (Me_2SO) 10.75 (s), occurred within a few minutes when pure HCO_2H[8] was added to a dil. CH_2Cl_2 soln. of (*Z*)-(**4**), (*E*)-(**4**), or a mixture of the two isomers.

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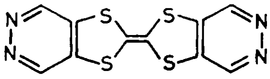
† Poster communications: A. Gorgues and A. Le Coq, Journées de Chimie Organique de la Société Chimique de France, Palaiseau, France, Sept. 15, 1981; A. Gorgues, P. Batail, and A. Le Coq, International CNRS Colloquium on the Physics and Chemistry of Synthetic and Organic Metals, les Arcs, Bourg Saint Maurice, France, Dec. 17, 1982.

‡ Satisfactory spectral data have been obtained for all new compounds (i.r., ^1H n.m.r., u.v.–vis., and mass spectrometry).

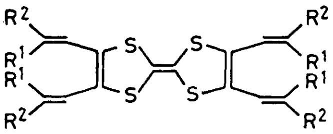
§ Additional structural evidence for (**3**) was provided by quantitative conversion into the corresponding dialdehyde,‡ yellow crystals, m.p. 124 °C (decomp.).



(6)

$$Ph_3\overset{+}{P}-\overset{-}{C}R^1R^2$$

(7a–e)



(8a–e)

a; $R^1 = H, R^2 = CO_2Et$
b; $R^1 = H, R^2 = Ac$
c; $R^1 = H, R^2 = Ph$
d; $R^1 = R^2 = Me$
e; $R^1 = R^2 = H$

We took advantage of the four aldehyde groups to synthesise the bispyridazino-TTF, (**6**), [yellow powder, m.p. 300 °C (decomp.), i.r. (Nujol) 1660 cm^{-1}, ^1H n.m.r. (Me_2SO) 9.78 (s)] in one step by treatment with $N_2H_4.H_2O$ in *N*,*N*-dimethylformamide (80% yield). We then decided to build the tetravinyltetrathiafulvalene derivatives (**8a**—**e**) through Wittig reactions. The feasibility of this was first tested by using stabilized P-ylides (**7a**—**c**) which, indeed, gave the corresponding (**8a**—**c**), exhibiting the expected poor π-donor ability.¶ By contrast, condensation of (**5**) with the very reactive (**7d**)[9] afforded (**8d**) (35% yield) [yellow needles, m.p. 114—115 °C (recrystallization from MeOH or EtOH), ^1H n.m.r. (CCl_4) 1.83 (d, *J* 1.2 Hz) and 5.72 (m, *J* 1.2 Hz)] which is as good a donor as TTF** as demonstrated by its 1 : 2 complexation with tetracyanoquinodimethane to give a dark blue polycrystalline semiconductor [compressed powder conductivity[10] 0.5 Ω^{-1} cm^{-1}, m.p. 180—185 °C (decomp.), recrystallised from tetrahydrofuran–Et_2O].

Attempts to isolate the even more attractive tetravinyltetrathiafulvalene (**8e**) have so far been unsuccessful owing to its rapid polymerisation.

We thank Dr. E. Torreilles and Dr. J. B. Torrance for stimulating discussions and Prof. R. Granger for a preliminary conductivity measurement.

Received, 5th January 1983; Com. 026

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7 G. Le Coustumer and Y. Mollier, *J. Chem. Soc., Chem. Commun.*, 1980, 38. As previously noticed in other experiments by H. Alper and H. N. Park, *J. Org. Chem.*, 1977, **42**, 3522 we observed (thin layer chromatography) the formation of transient organometallic species which thermally evolve into (**5**).

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10 Temperature dependent conductivity and thermo-power measurements showed this material to be a semiconductor with a rather small band gap (0.06 eV); electrons are the main carriers (S = —54 V K^{-1} at 300 K), P. Batail and R. L. Greene, unpublished results. This was further confirmed by i.r. spectroscopy which gives a gap of *ca.* 700 cm^{-1}; A. Girlando, personal communication.

¶ (**8b**): $E_1^{1/2} = 0.78$, $E_2^{1/2} = 0.95$ V *vs.* standard calomel electrode (S.C.E.); (**8c**): $E_1^{1/2} = 0.42$, $E_2^{1/2} = 0.67$ V *vs.* S.C.E.; MeCN, Bu_4NClO_4 electrolyte.

** $E_1^{1/2} = 0.33$, $E_1^{1/2} = 0.65$ V *vs.* S.C.E. (0.32 and 0.70, respectively for TTF); MeCN, Bu_4NClO_4 electrolyte. We thank A. Darchen for these measurements.