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Synthetic Method for the Preparation of Monosubstituted Tetrathiafulvalenes

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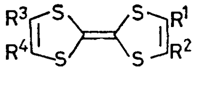
Summary Monosubstituted tetrathiafulvalenes and their selenium analogues have been prepared by the formation of tetrathiafulvalenyl-lithium (**2**) and the subsequent reaction with CO_2 or trialkyloxonium salts.

CHARGE-TRANSFER salts of tetrathiafulvalene (TTF) (**1**) and its derivatives have been shown to possess the highest electrical conductivity known of organic solids.[1] Recent work on altering the conducting properties of these charge-transfer salts has centred around the preparation of new derivatives of TTF and its selenium analogue TSeF,[2] usually by coupling of appropriately substituted cyclic 1,3-dithiol-2-thiones or their dithiolium salts. However these methods and other known methods for the preparation of TTF derivatives[3] lack the versatility to introduce a large variety of substituents into TTF, especially in the case of monosubstituted derivatives as shown by their absence from the literature. Direct substitution methods such as chlorination have yielded only the radical-cation salts or dication salts.[4]



(**1**); $R^1=R^2=R^3=R^4=H$
(**2**); $R^1=Li, R^2=R^3=R^4=H$
(**3**); $R^1=CO_2H, R^2=R^3=R^4=H$
(**4**); $R^1=CO_2Et, R^2=R^3=R^4=H$
(**5**); $R^1=R^{3(4)}=CO_2Et, R^2=R^{4(3)}=H$
(**6**); $R^1=R^2=R^3=R^4=CO_2Me$
(**7**); $R^1=Et, R^2=R^3=R^4=H$

We now report a general method for the preparation of monosubstituted TTF derivatives, involving the formation of the lithium derivative (**2**) by the reaction of BuLi with (**1**) and subsequent reaction of (**2**) with reagents such as CO_2. The acid (**3**) was thus prepared in 56% yield, m.p. 182—184 °C (decomp.), i.r. (KBr) 1660 (C=O) cm^{-1}; δ [$(CD_3)_2CO$, Me_4Si reference] 7·6 (1H, s, CH), 6·7 (2H, s, CH), and 5·35 (1H, s, CO_2H). The ethyl ester (**4**) of (**3**) was also prepared, m.p. 79—80 °C, i.r. (KBr) 1690 (C=O) cm^{-1}, δ (CCl_4) 7·3 (1H, s, CH), 6·3 (2H, s, CH), 4·25 (2H, q, J 7 Hz, CH_2), and 1·35 (3H, t, J 7 Hz, Me). The presence of one electron-withdrawing carboxylate functional group on TTF does not seriously detract from its electron donor properties as shown by a comparison of its electrochemical oxidation potentials with those of the known higher substituted homologues (Table), and by the formation of a highly conducting charge-transfer salt of (**3**) with tetracyanoquinodimethane (room-temperature compressed-pellet conductivity 8·3 Ω^{-1} cm^{-1}). Thus monofunctionalization of TTF allows it to be attached to other molecular systems in order to impart its unique electron donating properties to such systems.

TABLE

Oxidation potentials of donor molecules[a]

Compound	E_1	E_2	Ref.
(**1**)	0·34	0·71	b
(**3**)	0·47	0·83	This work
(**4**)	0·47	0·83	This work
(**5**)	0·60	0·94	c
(**6**)	0·80	1·08	c

[a] All potentials are peak potentials *vs.* S.C.E., Pt electrode, MeCN, 0·1M Et_4NClO_4, 0·2 V s^{-1}. [b] Ref. 4. [c] C. U. Pittman, M. Narita, and Y. F. Liang, *J. Org Chem.*, 1976, **41**, 2855.

The tetraselafulvalene analogue of (**3**) was prepared similarly, m.p. 165 °C (decomp.); i.r. (KBr) C=O 1670 cm^{-1}; E_1 + 0·63 V, E_2 + 0·90 V. Similarly, reaction of (**2**) with

Et_3OPF_6 yielded (**7**), yellow oil, δ (CCl_4) 7·3 (2H, s, CH), 5·8 (1H, s, CH), 2·45 (2H, q, *J* 8 Hz, CH_2) and 1·25 (3H, t, *J* 7 Hz, Me); E_1 + 0·33 and E_2 + 0·70 V.

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