A Modified Synthesis of Tetraselenafulvalenes

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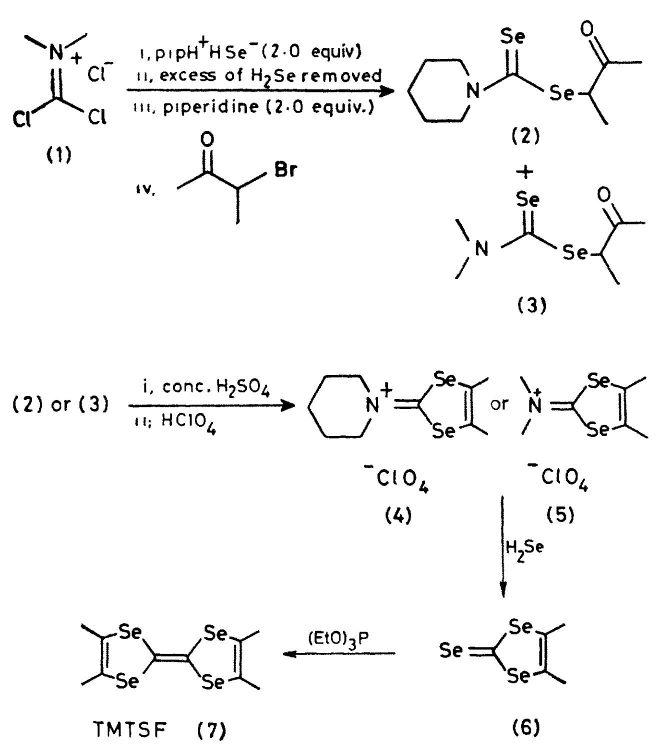
Summary Substituted tetraselenafulvalenes can be prepared in a four-step synthesis starting with dichloromethylene(dimethyl)ammonium chloride, hydrogen selenide, and an organic base

TETRATHIAFULVALENES[1] and tetraselenafulvalenes[2] form a class of electron donors whose salts are crystallographically similar, but which range in electrical behaviour from Mott and Peierls' insulators to nearly one-dimensional metals [3] The latter include the hexafluorophosphate salt of tetramethyltetraselenafulvalene $(TMTSF)_2PF_6$, recently found by Jerome, Bechgaard, and co-workers to be superconducting under modest pressure at low temperatures [4] We report here a modification of our previous synthesis[3,5] of TMTSF and related selenium π-donors that avoids the use of carbon diselenide and simplifies the large-scale preparation of these compounds

The synthetic route leading to TMTSF (**7**) is illustrated

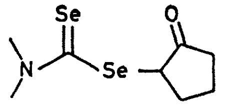


Scheme

in the Scheme. Dichloromethylene(dimethyl)ammonium chloride[6] (**1**) was treated with piperidinium hydrogen selenide (pipH$^+$HSe$^-$) (2·0 equiv. of dry piperidine, and an excess of hydrogen selenide) in dry CH_2Cl_2 for 1 h. The excess of hydrogen selenide was then removed and 2 equiv. of piperidine were introduced to generate the diselenocarbamate intermediate, which was subsequently allowed to react with an excess of 3-bromobutan-2-one to afford two major products (**2**)[2b] (23%) and (**3**) [(61%), δ ($CDCl_3$): 1·65 (d, 3H, *J* 8 Hz), 2·36 (s, 3H), 3·40 (s, 3H), 3·72 (s, 3H), and 5·14 (q, 1H, *J* 8 Hz); *m/e* 287 (M^+), 217 ($M^+ - C_4H_6O$), and 137 ($M^+ - C_4H_6O - Se$)].

Ring-closure of either (**2**) or (**3**) using the previously described method[2a,b] afforded the diselenolium salts (**4**) or (**5**) in 75% yield. Both the salts were treated further with hydrogen selenide in absolute methanol at −20 to −40 °C for 3 h to give the identical selone[2a,b] (**6**) in 95% yield. The coupling reaction of the selone (**6**) with an excess of triethyl phosphite in xylene at 140 °C for 5 h gave the known compound[2a,b] TMTSF (**7**).

When 2-bromocyclopentanone (from cyclopentanone and $CuBr_2$) was used in place of 3-bromobutan-2-one, a mixture of (**8**) and (**9**) was obtained in 42% yield. Ring-closure of this mixture proceeded in 60% yield. Treatment of the resulting diselenolium salts with hydrogen selenide afforded the selone (**10**) in 98% yield as a red crystalline solid,[2a,b] [δ ($CDCl_3$): 2·52 (q, 2H, *J* 7 Hz) and 2·90 (t, 4H, *J* 7 Hz)]. This selone can be converted into the known tetraselenafulvalene,[2a,b] HMTSF (**11**).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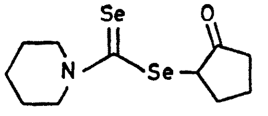
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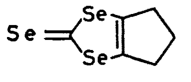
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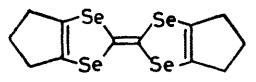
HMTSF (11)

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[1] (a) J. P. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948; (b) F. Wudl, D. Wobschall, and E. J. Hufnagel, *ibid.*, 1972, **94**, 670.

[2] (a) K. Bechgaard, D. O. Cowan, and A. N. Bloch, *J. Chem. Soc., Chem. Commun.*, 1974, 937; (b) K. Bechgaard, D. O. Cowan, A. N. Bloch, and L. Henriksen, *J. Org. Chem.*, 1975, **40**, 746; (c) E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, 1974, **96**, 7376.

[3] (a) D. Cowan, P. Shu, C. Hu, W. Krug, T. Carruthers, T. Poehler, and A. N. Bloch, in 'Chemistry and Physics of One-Dimensional Metals,' ed. H. J. Keller, Plenum Press, New York, 1977, pp. 25—46; (b) A. Bloch, T. Carruthers, T. Poehler, and D. Cowan, *ibid.*, pp. 47—85; (c) J. P. Stokes, A. N. Bloch, W. A. Bryden, D. O. Cowan, M. E. Hawley, and T. O. Poehler, *Bull. Am. Phys. Soc.*, 1977, **24**, 232.

[4] D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, *J. Phys. Lett.* (*Paris*), 1980, 15.

[5] P. Shu, A. N. Bloch, T. F. Carruthers, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 1977, 505; the procedure described in this paper gives high yields of the diselenadithiafulvalenes but lower yields of the tetraselenafulvalenes.

[6] H. G. Viehe and Z. Janousek, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 573.