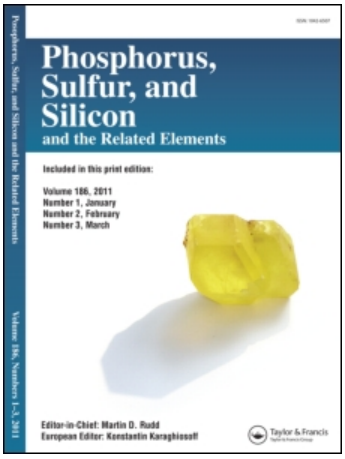

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THIAPEN CHEMISTRY: CAPPING REACTIONS OF THIAPENDIONE

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THIAPEN CHEMISTRY: CAPPING REACTIONS OF THIAPENDIONE

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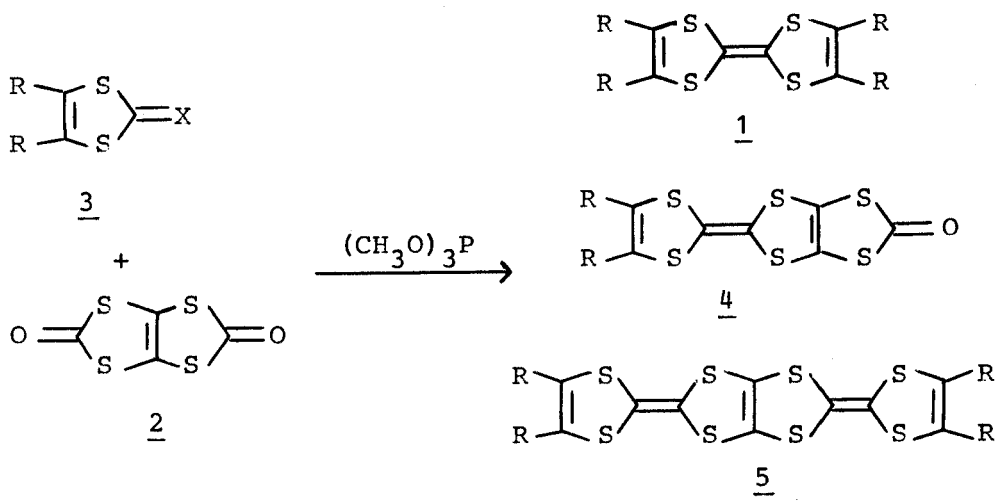
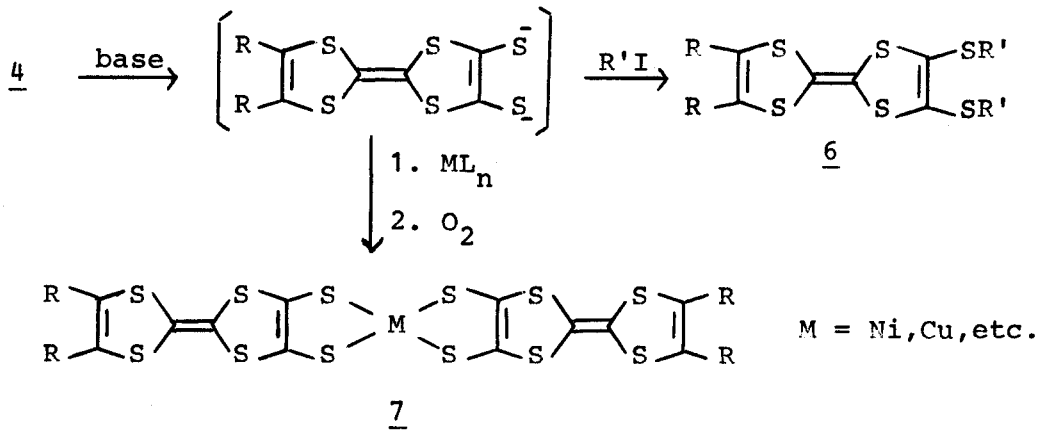
Considerable interest has been shown in the chemistry of tetrathiafulvalene (TTF, 1) since some of these π-donors react with acceptors to form the most conducting organic solids presently known.[1] The recent synthesis of thiapendione (2)[2] provided the possibility of elaborating a wide variety of novel TTF derivatives through cross-coupling reactions with 1,3-dithioles (3) using trimethyl phosphite. The capping reaction is very dependent on the nature of the R and X



substituents in 3, and succeeds for R=CN, X=0 or R= CO_2Me, CF_3, X=S to give mono- and bis-capped products 4 and 5.

Mono-capped products (4) react with base to provide dithiolate intermediates which can be quenched with alkyl iodides to afford a variety of unsymmetrically substituted tetrathiafulvalenes (6), or with transition metal salts to give a new class of metal bis-dithiolene derivatives (7) which incorporate TTF as a conjugated ligand.



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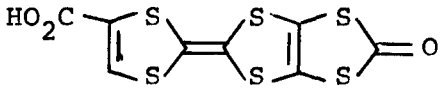
Cross-coupling of 2 with 1,3-diselenole-2-thione analogs of 3 results in an interchange of a ring selenium with the carbonyl sulfur before capping to 2. The self-coupled product also shows this sulfur-selenium rearrangement.[3]

Treatment of 4 (R=CN, CO_2Me) with concentrated acid at elevated temperatures affects hydrolysis and decarboxylation to give mono-acid 8.



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2. R. R. Schumaker and E. M. Engler, J. Am. Chem. Soc. 99, 5519, 5521 (1977).

3. E. M. Engler, V. V. Patel and R. R. Schumaker, J. Chem. Soc., Chem. Comm., 835 (1977).