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THIAPEN CHEMISTRY: CAPPING REACTIONS OF THIAPENDIONE

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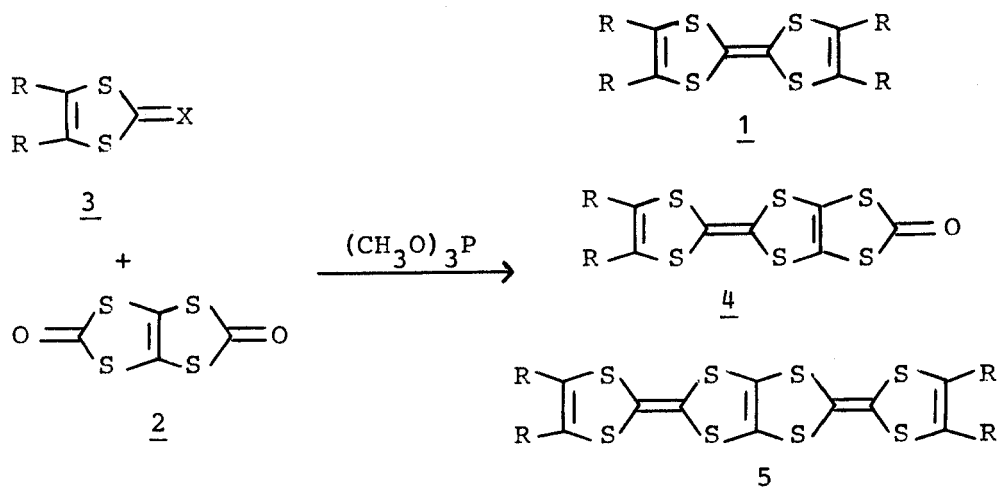
THIAPEN CHEMISTRY: CAPPING REACTIONS OF THIAPENDIONE

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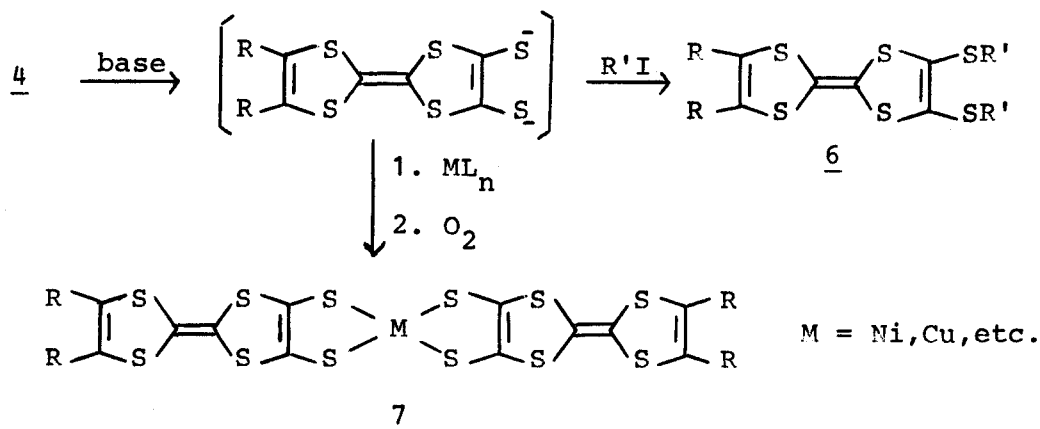
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Considerable interest has been shown in the chemistry of tetrathiafulvalene (TTF, 1) since some of these π -donors react with acceptors to form the most conducting organic solids presently known.¹ The recent synthesis of thiapendione (2)² provided 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



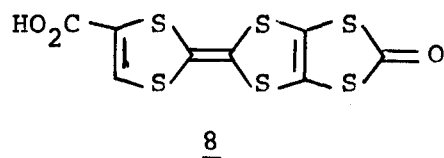
substituents in 3, and succeeds for $R=CN$, $X=O$ or $R=CO_2Me$, CF_3 , $X=S$ to give mono- and bis-capped products 4 and 5.

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.



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 self₃coupled product also shows this sulfur-selenium rearrangement.

Treatment of 4 (R=CN, CO₂Me) with concentrated acid at elevated temperatures affects hydrolysis and decarboxylation to give mono-acid 8.



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