SYNTHESIS OF TETRATHIOFULVALENES

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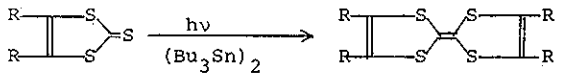
A new useful photochemical one-step process for the preparation of the title compounds is reported. A benzene or hexane solution of various 1,3-dithiole-2-thiones was irradiated with 300-W high pressure mercury lamp for 5 hr in the presence of equimolar amount of hexabutyldistannane to give tetrathiofulvalenes in good yields(50-77%).



[R=CH_3, $-(CH_2)_2-$, $COOCH_3$, Ph]

Controlled experiments revealed that the rate enhancement was observed at wavelengths which correspond to the absorptions of thiones. A possible reaction mechanism is described.

A convenient method for the preparation of 4,5-unsubstituted 1,3-dithiole-2-thione, which is the key intermediate in TTF synthesis, is also reported.

The polymer which contains TTF unit in the main chain was prepared by the poly-dimerization of bis-S,S-carbene. The polymer obtained formed the complex with tetracyanoquinodimethane or 2,3-dichloro-5,6-dicyanobezoquinone.