

SYNLETT Spotlight 431

β -Oxodithioesters

Compiled by Girijesh Kumar Verma



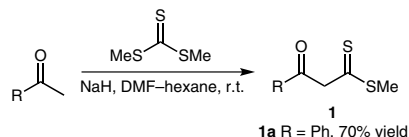
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Girijesh Kumar Verma was born in Deoria (India) in 1984. He received his B.Sc. (2005) and M.Sc. (2007) in Chemistry from Deen Dayal Upadhyay Gorakhpur University (India). He is currently pursuing his Ph.D. under the supervision of Professor M. S. Singh at Banaras Hindu University, Varanasi (India). His current research interest is focused on the use of ketene-*S,S*-/*N,S*-acetals and β -oxodithioesters.

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Introduction

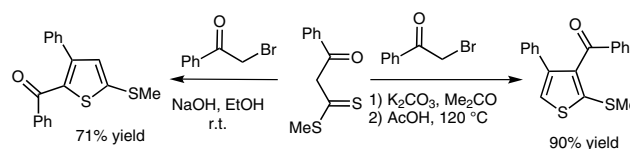
β -Oxodithioesters **1**, sulfur analogues of β -ketoesters, are important synthons frequently used for the synthesis of heterocycles. **1** can easily be synthesized by the reaction of methyl ketones (or active methylene compounds) with dialkyl-, allyl-, or benzyl trithiocarbonates in the presence of NaH (Scheme 1).¹ These versatile reagents are yellow and have a low melting point as well as an offensive odor.



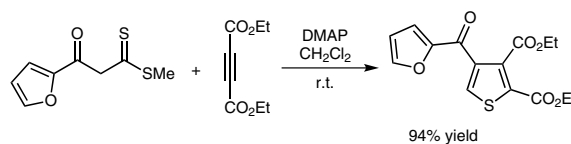
Scheme 1 Synthesis of β -oxodithioesters

Abstracts

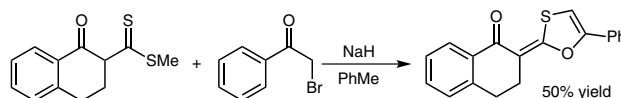
(A) Samuel et al.⁴ reported the synthesis of thiophenes by alkylation of β -oxodithioester with α -haloketones. Depending on the combination of base and solvent, differently substituted thiophenes are obtained.



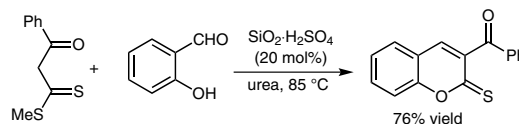
(B) β -Oxodithioester in the presence of DMAP reacted with dialkyl acetylenedicarboxylate to give 2,3,4-trisubstituted thiophenes in high yield in short reaction times.⁵



(C) Samuel et al.⁶ have reported the synthesis of 2-ylidene-1,3-oxathioles in good yield using β -oxodithioester and α -haloketone in the presence of NaH in toluene.



(D) Chromene and benzochromene-2-thiones were efficiently synthesized in high yield by the reaction of β -oxodithioester and 2-hydroxy benzaldehyde/naphthaldehyde under solvent-free conditions using $\text{SiO}_2 \cdot \text{H}_2\text{SO}_4$ as the catalyst.⁷



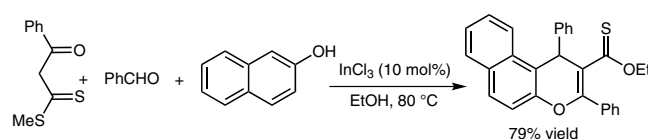
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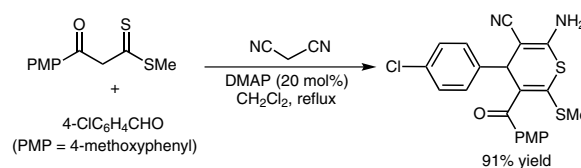
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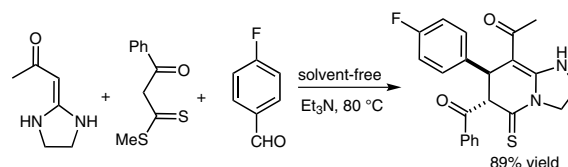
(E) A facile and efficient protocol for the synthesis of benzo[*f*]chromene from β -oxodithioester and β -naphthol has been developed using catalytic InCl_3 . In this reaction, transesterification was also observed.⁸



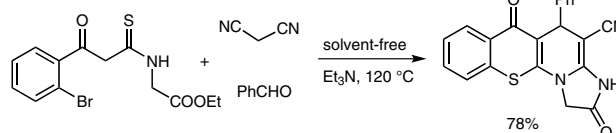
(F) Singh et al.⁹ have presented the synthesis of highly functionalized thiopyran/thiochromene derivatives when β -oxodithioester was treated with aldehyde and an active methylene compound containing a cyano group^{9a} or a 1,3-cyclohexanedione.^{9b}



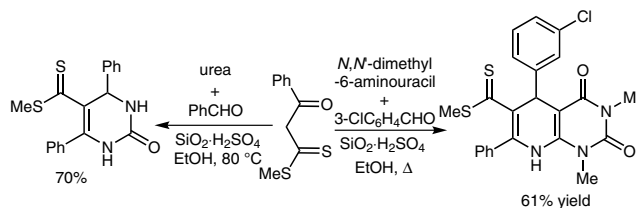
(G) A green and highly efficient method for the regioselective synthesis of imidazo[1,2-*a*]pyridine derivatives using β -oxodithioester, cyclic *N,N*-acetal and aldehyde has been presented by Li and co-workers.¹⁰



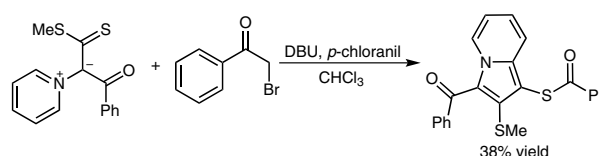
(H) Li and co-workers¹¹ also reported an unprecedented, three-component cascade synthesis of imidazo[1,2-*a*]thiochromeno[3,2-*e*]pyridines under solvent-free conditions without using any transition-metal catalyst.



(I) Dihydropyrimidinones and dihydropyridopyrimidinones were synthesized via one-pot, three-component cyclocondensation of aromatic aldehydes, β -oxodithioesters, and urea/6-amino-1,3-dimethyluracil in the presence of a recyclable $\text{SiO}_2\text{-H}_2\text{SO}_4$ acid catalyst.⁷



(J) The treatment of pyridine substituted β -oxodithioester with 2-bromoacetophenone led to the formation of highly substituted indolizine in moderate to good yield. The reaction was performed in chloroform in the presence of catalyst DBU/*p*-chloranil. Kakehi et al.¹² have synthesized and analyzed the conformation of these molecules.



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