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

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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

Other synthons such as β -oxothioamides and *S,S*- or *N,S*-acetals can also be synthesized from **1**.^{2,3} Figure 1 shows the reactivity profile of β -oxodithioesters: the carbon atoms of the carbonyl and thiocarbonyl groups are electrophilic centers while oxygen, sulfur, and the carbon of the active methylene group are nucleophilic centers.

Figure 1 Reactivity profile 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

(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 $\text{SiO}_2 \cdot \text{H}_2\text{SO}_4$ 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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