Spotlight 431

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

β-Oxodithioesters

Compiled by Girijesh Kumar Verma

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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

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

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(E) A facile and efficient protocol for the synthesis of benzof[1]chromene from β-oxodithioester and β-naphthol has been developed using catalytic InCl₃. 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 group⁹a or a 1,3-cyclohexanedione.⁹b

(G) A green and highly efficient method for the regioselective synthesis of imidazo[1,2-a]pyridines under solvent-free conditions without using any transition-metal catalyst.

(H) Li and co-workers¹⁰ also reported an unprecedented, three-component cascade synthesis of imidazo[1,2-a]thiophenes[3,2-e]pyridines when a cyano group⁹a or a 1,3-cyclohexanedione.⁹b treated with aldehyde and an active methylene compound containing a cyano group⁹a or a 1,3-cyclohexanedione.⁹b

(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 SiO₂·H₂SO₄ 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.

References