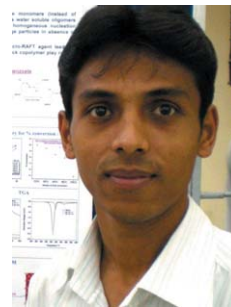


SYNLETT Spotlight 317

Thiocarbonylthio Compounds

Compiled by Niranjn Yeole



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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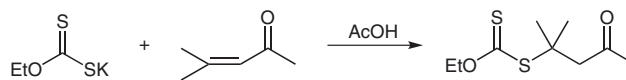
Introduction

Thiocarbonylthio compounds consist mainly of thioesters, trithiocarbonates, xanthates, and dithiocarbamates. They undergo saponification, alcoholysis or aminolysis in the same way as carbonates, carbamates and carboxylic esters. Xanthates and dithiocarbamates con-

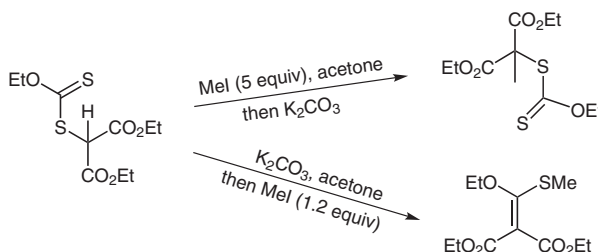
cern vulcanization of rubber and in formulation of insecticides and fungicides for plant protection. Also, these compounds are used as agents for the reversible addition fragmentation chain transfer (RAFT) in controlled polymer synthesis. Thiocarbonylthio compounds can be achieved in moderate to high yield by heating a bis(thiocarbonyl) disulfide with an azo compound.¹

Abstracts

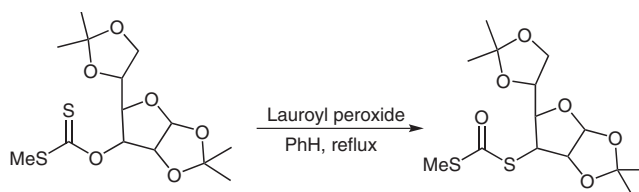
(A) Thiocarbonylthiol compounds are more acidic and therefore undergo β -eliminations under basic conditions. The efficient addition of xanthate to mesityl oxide in an acidic medium to avoid the reversible addition gives the product in 76% yield. Thus, tertiary derivatives can be accessed through a conjugate addition rather than by S_N2 substitution.²



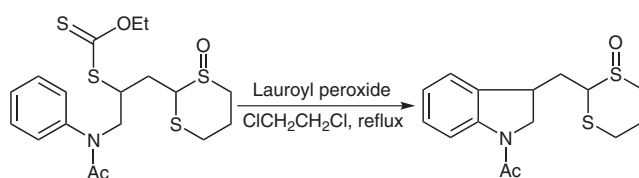
(B) The synthesis of tertiary xanthate by methylation of xanthate can be achieved by addition of an excess amount of the alkylating agent before adding the base. By inverting the mode of addition the ketene monothioether can be obtained.³



(C) Secondary alcohols can be converted into the corresponding thiols using this method. This method is convenient in cases where a traditional ionic approach is difficult to use.⁴ The radical generated using carbon-centered radical by proper selection of the various substituents and the experimental conditions, scission of the C–O bond is irreversible, and leads to an S,S' -dithiocarbonate.



(D) If xanthate is separately exposed to the action of peroxide, then there is no alternative other than generating radical, even if it is not particularly stabilized. This radical may add to aromatic ring giving the stabilized cyclohexadienyl radical. The radical is easily oxidized to the equally stable corresponding cation by electron transfer to the peroxide. Aromatization by loss of proton quickly yields indoline.⁵



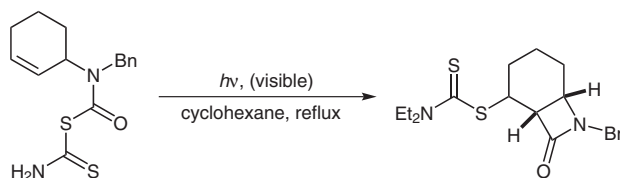
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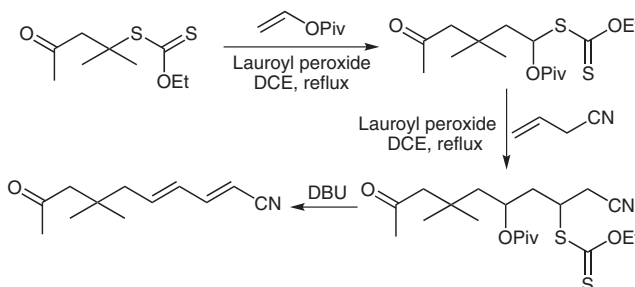
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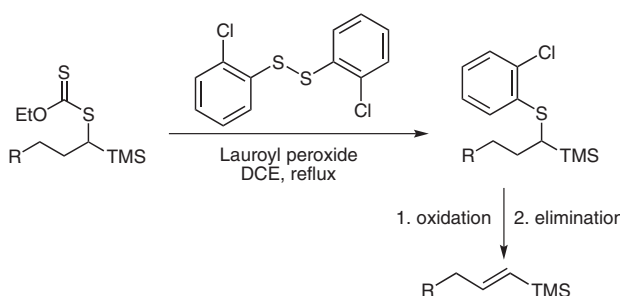
(E) For the generation and intramolecular capture of carbamoyl radicals, dithiocarbamates proved better than xanthates. The formation of the β -lactam from acyl dithiocarbamate via an acyl radical has been reported by Grainger and Innocenti. Lactams of various sizes were prepared by the same approach.⁶



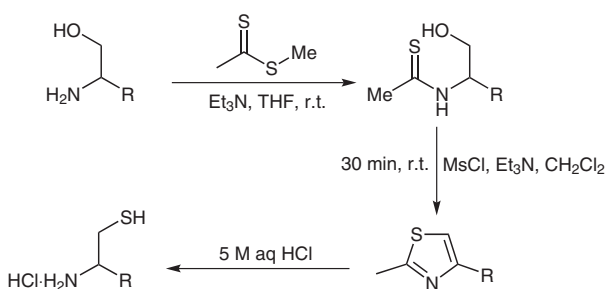
(F) When xanthate is added to vinyl pivalate, a related adduct is further reacted with allyl cyanide. The expected adduct is not isolated but exposed to the action of a base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which causes two successive β -eliminations leading to the diene.⁷



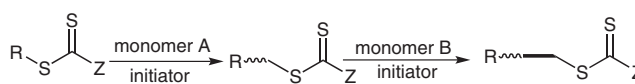
(G) Xanthates have been readily converted into *ortho*-chlorophenyl thioethers using a one-step procedure and radical conditions. In some cases, the aryl thioethers are successfully oxidized to the corresponding sulfoxides and sulfenic acid elimination afforded the corresponding vinylsilanes.⁸



(H) Various primary 2-aminothiols have been prepared in three steps starting from 2-aminoalcohols and methyl dithioacetate.⁹



(I) The use of thiocarbonylthio compounds in radical polymerizations is a versatile method for conferring living characteristics providing unprecedented control over molecular weight, molecular weight distribution, composition, and architecture. It provides a route to functional, cyclo-, block, and star polymers as well as to gradient copolymers.¹⁰



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