

SYNLETT Spotlight 274

Malonyl Dichloride

Compiled by Leandro José dos Santos



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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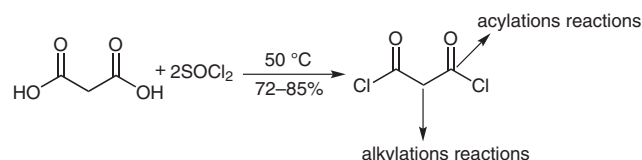
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Introduction

Malonyl dichloride, or malonyl chloride $\text{CH}_2(\text{COCl})_2$, is widely used in organic synthesis as a versatile biselectrophilic reagent. This compound has been used mainly in acylation (O-, S-, N-, C-acylation) and alkylation reactions. It is a convenient reagent for the preparation of heterocyclic derivatives¹⁻⁸ and is utilized as an important building block in the synthesis of supramolecular compounds⁹⁻¹² with several applications. An attractive use of malonyl dichloride is the formation of the bicyclo[3.3.1]nonane-trione system¹³⁻¹⁵ in a one-pot reaction. Compounds containing this bicyclo system are common features incorporated into the structures of numerous natural products. Malonyl dichloride must be handled with precaution because it is lachrymating and corrosive. Due to the reaction with water it decomposes when exposed to wet air.

Preparation

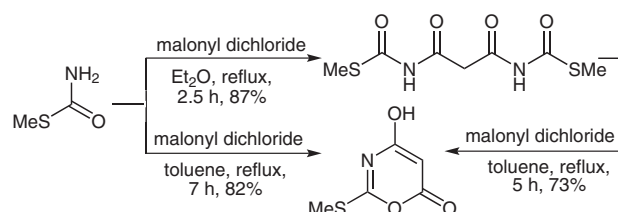
The commercially available malonyl dichloride can be synthesized from malonic acid using thionyl chloride (Scheme 1).^{16,17} A pale yellow liquid is obtained after its purification.



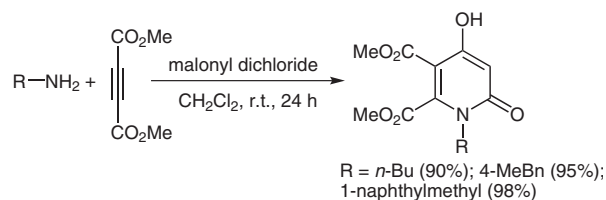
Scheme 1

Abstracts

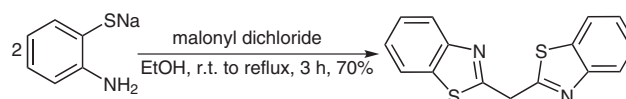
(A) The reaction of methyl thiocarbamate with malonyl dichloride in dry diethyl ether provides an N-substituted thiocarbamate. When this reaction is performed at high temperatures in dry toluene, it leads to oxazinone.¹ Oxazinone can be prepared from thiocarbamate by treatment with 1 mol% of malonyl dichloride.¹



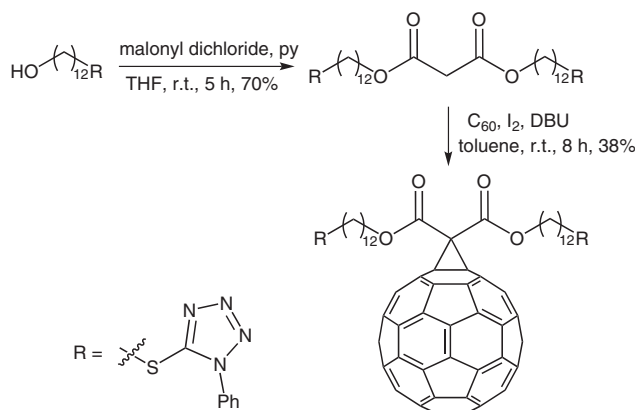
(B) The multicomponent condensation between alkylamines, dimethyl acetylenedicarboxylate in the presence of malonyl dichloride has been recently reported by Yavari and Sourì for the formation of the functionalized 2-pyridones in good yields.²



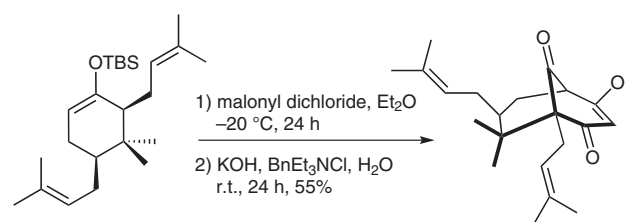
(C) Karaböcek et al. reported a new method for the preparation of benzothiazole involving a one-step reaction between malonyl dichloride and 2-amino thiophenol sodium salt in absolute ethanol.³



(D) Malonyl dichloride has been used as an important building block in the synthesis of stable [6,6]-closed cycloadducts of [60]fullerene. The first step, O-acylation, gives the corresponding malonate, and is followed by cyclopropanation through Bingel-type chemistry.⁹



(E) Effenburger-type cyclization affords very rapid and elegant access to an appropriate bicyclo[3.3.1]nonane-trione system in a one-pot reaction. The desired product can be formed diastereoselectively by reacting either cyclohexanone-derived enol ethers or enol silanes with malonyl dichloride, followed by a basic workup.¹³



References

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