SYNLETT Spotlight 316

2-Chloro-1,3-Dimethylimidazolinium Chloride

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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

2-Chloro-1,3-dimethylimidazolinium chloride (DMC) is a commercial chloroamidinium salt that has been widely used as a dehydrating reagent in organic synthesis. The synthetic importance and significance of DMC is based on its simple preparation from 1,3-dimethyl-2-imidazolidinone (DMI) by chlorination and on the easy removal of regenerated DMI after its condensation reaction by washing with water (Scheme 1). Compared with the traditional dehydrating reagents, such as dicyclohexylcarbodiimide

(DCC) and *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide (EDCI), DMC is a low-cost and significant non-toxic reagent.¹ On the other hand, DMC associated with its excellent character has been widely used in some multistep reactions for the synthesis of complex compounds.^{2–5}

Scheme 1

Abstract

(A) Node et al. reported a facile and efficient synthesis of allene-1,3-dicarboxylates. The reaction of acetone-1,3-dicarboxylates with DMC and triethylamine was performed in dichloromethane at room temperature using intermediates of vinyl chloride to afford the corresponding allenes in good to excellent yields.⁶

(B) Isobe and co-workers developed a new method for the synthesis of guanidines by DMC-induced cyclizations of protected thiourea intermediates derived from the corresponding chiral ethylenediamines. The simple synthetic approach to 1,3-unsubstituted and 1-substituted 2-iminoimidazolidines was explored for new chiral superbases.^{7,8}

(C) Isobe et al. demonstrated an alternative cyclization of modified guanidines by using appropriate 2-amino alcohols. The key step of this strategy was the substitution of the hydroxyl group through a chlorine atom catalyzed by DMC. The successful preparation of cyclic guanidines resulted in uncovering further utility of DMC in organic synthesis.⁹

(D) An efficient DMC-catalyzed dehydration cyclization between carboxylic acids and various imines was developed. On the basis of this intermolecular condensation, a series of β -lactams was prepared in high to excellent yields. Moreover, this reaction exhibited obvious stereochemistry by using substituents present on the carboxylic acids.¹⁰

(E) Sakurai described an efficient cyclodehydration of γ -keto acid derivatives, which afforded the corresponding five-membered heterocycles in the presence of DMC.^{11a} In addition to mild conditions, simple procedure, and high yields, this method provided a convenient protocol for the synthesis of corresponding γ -imino- α,β -butenolides through an intramolecular condensation when maleic acid monoamides were used as starting materials.^{11b,c}

(F) Functionalized benzoxazinones were synthesized from *N*-acyl-anthranilic acids in the presence of DMC through a cyclodehydration process. It is of great interest to note that the presented annulation is associated with mild conditions, simple execution, and good yields.¹²

(G) Fürstner et al. developed a novel method for the synthesis of palladium complexes bearing N-heterocyclic carbene (NHC) ligands using the oxidation addition of $Pd(PPh_3)_4$ to DMC. This strategy allowed for the direct exchange of the metathetic ligand without changing the oxidation state of the involved metal center, which was complementary to the existing methodologies.¹³

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