

SYNLETT Spotlight 195

Oxalyl Chloride: A Versatile Reagent in Organic Synthesis

Compiled by David Rodrigues da Rocha



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

David Rodrigues da Rocha was born in Rio de Janeiro, Brazil in 1981. He received his Industrial Pharmacy degree from Universidade Federal Fluminense in 2005 and his M.Sc. in Chemistry from Universidade Federal Fluminense in 2006. He is currently working toward his Ph.D. under the supervision of Prof. Vitor F. Ferreira and Prof. Wilson da C. Santos. His research interests focus on the synthesis of aminoalcohols and triazoles derived from carbohydrates.

Instituto de Química, Universidade Federal Fluminense, CEP: 24020-150, Niterói, Rio de Janeiro, Brazil
E-mail: davidrocha@uol.com.br

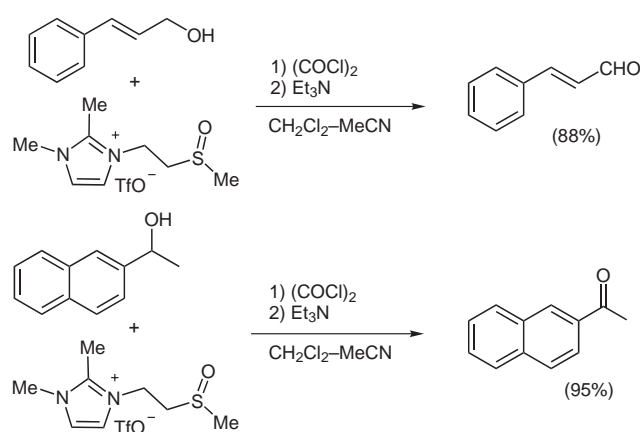
Introduction

Oxalyl chloride is a very versatile reagent extensively used by organic chemists. One of its most common uses is in oxidation of alcohols to aldehydes and ketones named Swern oxidation.^{1–5} However, this reagent can efficiently be applied in many other reactions such as 1,1-cycloaddi-

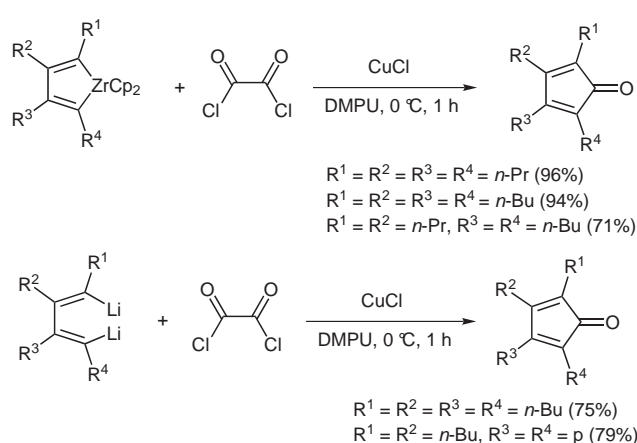
tions with 1,4-dilithio-1,3-dienes or zirconacyclopentadienes,⁶ cyclization of 1,3-bis(trimethylsilyloxy) alk-1-enes to isoelectronic acids,⁷ preparation of phenyl isocyanates from anilines,⁸ bicyclization of biaryl acetamides,⁹ dehydration of formamides to afford nitriles,¹⁰ and cyclization of 1,1-bis(trimethylsilyloxy) ketene acetals to give 3-hydroxymaleic anhydrides.¹¹

Abstracts

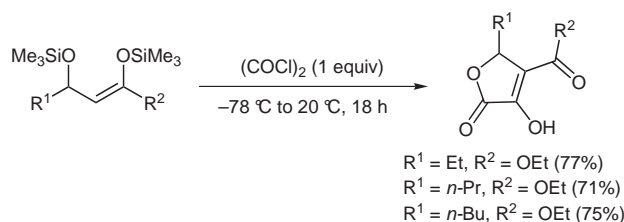
(A) He and Chan showed a new class of odorless and non-volatile organosulfur compounds anchored on imidazolium ionic liquid, which can be used effectively for the oxidation of alcohols to aldehydes and ketones in the presence of oxalyl chloride¹ under Swern oxidation conditions.²



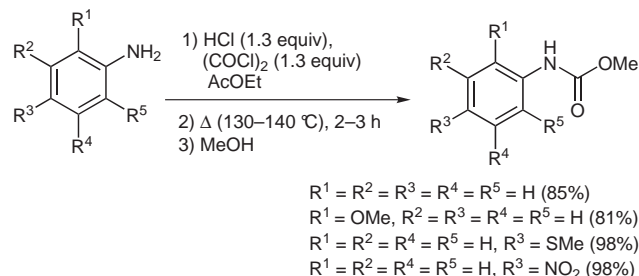
(B) Chen and workgroup reported a 1,1-cycloaddition of oxalyl chloride with 1,4-dilithio-1,3-dienes or zirconacyclopentadienes in the presence of CuCl and DMPU to afford cyclopentadienone derivatives in good yields.⁶



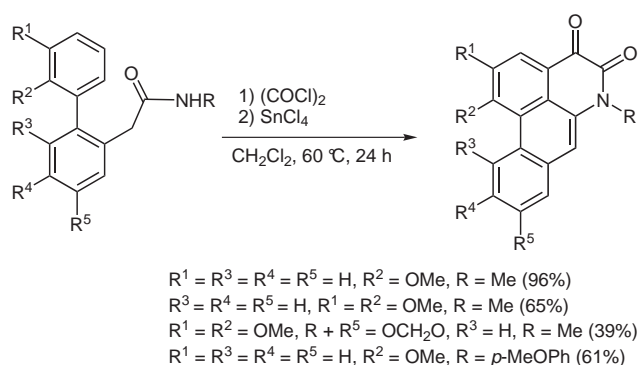
(C) Dede et al. showed a regioselective preparation of isoelectronic acids by cyclization of 1,3-bis(trimethylsilyloxy)alk-1-enes with oxalyl chloride in moderate yields.⁷



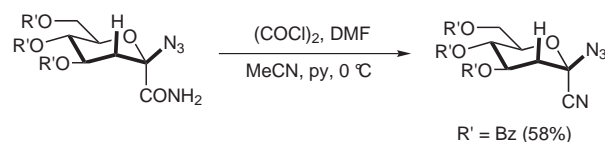
(D) Oh et al. reported a new and convenient method of generating phenyl isocyanates from anilines using oxalyl chloride. Acylation of a variety of substituted aniline hydrochlorides with oxalyl chloride affords the intermediate oxamic chlorides, which smoothly undergo thermal decomposition to the corresponding desired products.⁸



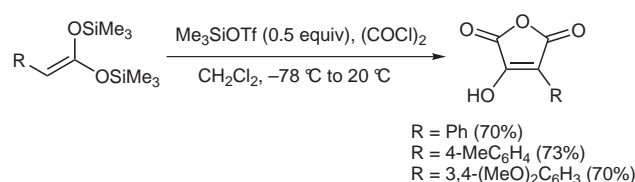
(E) Suau et al. showed that oxalyl chloride is a good promoter for bicyclization of a variety of biarylacetamides in the presence of SnCl_4 , which were used for the synthesis of aporphinoids.⁹



(F) Czifrák et al. reported a dehydration of per-O-benzoylated C-(1-azido-1-deoxy- α -D-glucopyranosyl)formamide by oxalyl chloride/DMF to give the corresponding nitrile in moderate yields.¹⁰



(G) Ehsan and Langer reported the use of oxalyl chloride in the synthesis of functionalized 3-hydroxymaleic anhydrides by cyclization of 1,1-bis(trimethylsilyloxy)ketene acetals.¹¹



References

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