

SYNLETT Spotlight 229

Dimethyldioxirane (DMD)

Compiled by Vishnu Prabhakar Srivastava



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

Vishnu Prabhakar Srivastava was born in Kushinagar, U. P., India in 1983. He received his B.Sc. (2003) and M.Sc. (2005) degrees in Organic Chemistry from D. D. U. Gorakhpur University, U. P.; then he worked as a research chemist in Chembiotek Research International Pvt. Ltd. Kolkata for one year before joining the research group of Prof. L. D. S. Yadav for his doctoral studies. His research interest focuses on the development of new synthetic methodologies for bioactive heterocycles, especially by employing the principles of green chemistry.

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Dedicated to my honorable mentor Prof. L. D. S. Yadav

Introduction

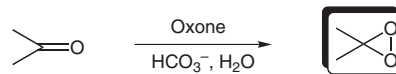
Dimethyldioxirane (DMD), a nonmetal organic oxidant, has the ability to transfer an oxygen atom to a wide range of substrates and functionalities, including C=C and C–H bonds in hydrocarbons as well as atoms containing lone pairs such as sulfide,¹ primary and secondary amines.² This nonmetal electrophilic oxygen transfer agent is the reagent of choice for most epoxidation reactions (better than MCPBA) due to its substrate-induced selectivity, specificity, and reactivity under mild conditions (at 0–25 °C and neutral pH). It reacts rapidly and in high yield, is easy to handle and applicable to acid- or base-sensitive substrates, and it can be used to synthesize hydrolytically labile oxyfunctionalized products.^{3–4}

DMD-mediated halogenations,^{5a} hydroxylations,^{5b} and oxidations are widely used in the chemistry of flavonoids,

low-molecular-weight natural compounds and in expanding the organoborane chemistry.^{6a,b} It also acts as a G-specific chemical sequencing agent and is a new source of singlet oxygen generation.^{7a,b}

Preparation

DMD is easily prepared by oxidizing acetone with commercially available low-cost potassium peroxydisulfate KHSO₅ (Oxone, Caroate) in water buffered at pH 7–7.5 using NaHCO₃ (Scheme 1). It is obtained as yellow solution in acetone in the range of 0.07–0.09 M concentration and usually stored in the freezer (–25 °C).³

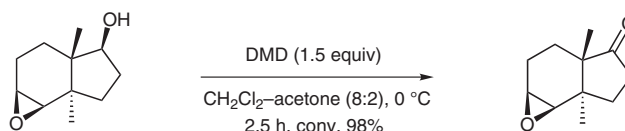


Scheme 1

Abstracts

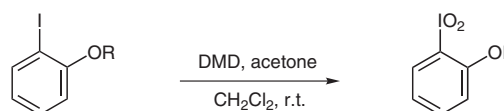
(A) Oxidation of Epoxy Alcohols:

Willard and co-workers have reported conversion of epoxy alcohols into their corresponding epoxy ketones in high yields by selective oxidation using DMD without affecting the configuration at the epoxy functionality.⁴



(B) Oxidation of Iodoarenes:

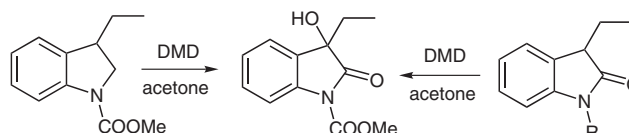
2-Iodoarylphenol ethers were prepared by DMD oxidation of corresponding 2-iodophenol ether and isolated as chemically stable, microcrystalline products.⁸



R = Me, Pr, *i*-Pr, Bu

(C) Oxidation of *N*-Substituted Indole and Oxyindole:

Suarez-Castillo et al. have developed a general and practical protocol for synthesizing 3-hydroxyoxindoles starting from indole and oxyindole derivatives. The methodology has been exploited to synthesize various medicinally important natural products.⁹



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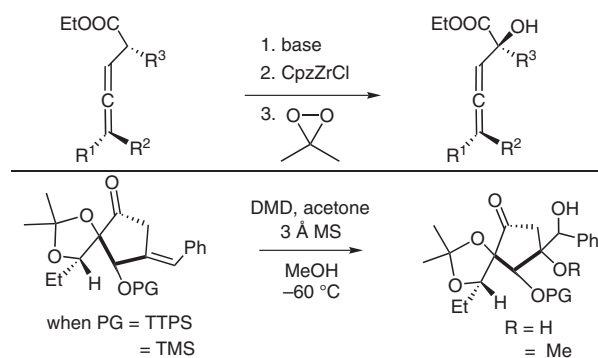
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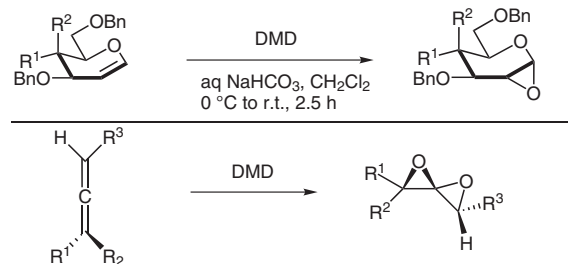
(D) Hydroxylation Reaction:

DMD selectively affords 2-hydroxy-3,4-dienoates by oxidizing zirconiumallanyl enolates^{10a} and oxidation of benzylidene derivatives with DMD in methanol leads to the formation of either 1,2-diol or monomethylated 1,2-diol governed by the adjacent crowding.^{10b}



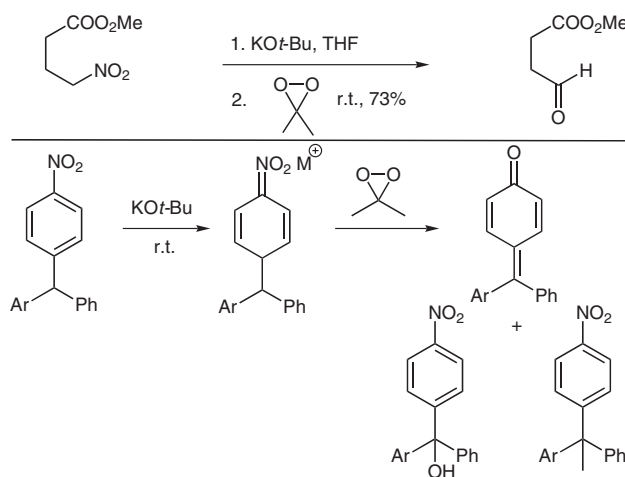
(E) Epoxidation Reactions:

Dondoni and co-workers have reported a multi-gram epoxidation of 3,4,6-tri-O-benzyl-D-glucal and D-galactal with DMD resulting in the formation of the corresponding 1,2-anhydrosugars in 99% yield and 100% stereoselectivity.^{11a} Recently, epoxidation of allene has been reported to give isolable SDEs (spiro-fused diepoxides).^{11b}



(F) Nef Reaction:

DMD selectively converts nitroalkanes into carbonyl compounds by oxidation at the nitronoate center (obtained by treatment of NO₂ with base).^{12a} Makosza et al. have reported oxidation of nitrobenzyl carbanions proceeding at the carbanion center to give hydroxyl compounds and at the nitronoate group to produce quinomethanes. The reaction course is governed by the substituent at the carbanion center and the reaction conditions: solvents and counteranion. In some cases, a peculiar reaction leading to methylation of the carbanion is observed.^{12b,c}



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