

SYNLETT Spotlight 143

Cerium(IV) Ammonium Nitrate: A Versatile Oxidant in Synthetic Organic Chemistry

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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

Amarajothi Dhakshinamoorthy was born in Tamil Nadu state in India in 1980. He received his B.Sc. degree in 2000 from Loyola College (affiliated to University of Madras) Chennai-34, India. He did his post-graduation work in chemistry with specialization in organic chemistry in 2002 from the same institute. He then joined the Sanmar Specialty Chemicals Research Centre (SSCRC), India as a research fellow. After one year of experience as researcher in SSCRC, he moved to the School of Chemistry, Madurai Kamaraj University as a research scholar to work under the supervision of Prof. K. Pitchumani for his Ph.D. Currently he is working in the area of organic chemistry, particularly in the synthesis of organic compounds using heterogeneous media, radical cyclizations mediated by cerium(IV) ammonium nitrate, and the development of environmentally benign procedures for their synthesis.

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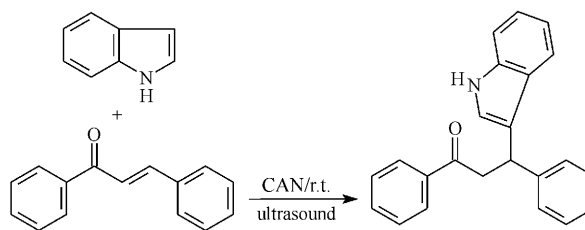
Introduction

Among the various cerium(IV) complexes, cerium(IV) ammonium nitrate (CAN) is one of the most important oxidants in organic synthesis, as it is sufficiently stable in different solvents and is commercially available. It is useful for introducing and removing protecting groups via single-electron transfer or Lewis acid catalysis.¹ CAN serves as a convenient reagent for the generation of radicals from CH-acidic substrates,² exhibiting a similar reactivity pattern (+1.61 V vs. NHE) as Mn(III) acetate (+1.51

V vs. NHE). Recently, CAN has been utilized for many synthetic transformations such as debenzoylation,³ oxidation,⁴ oxidative free-radical reactions in green media such as water⁵ and ionic liquids,⁶ carbon-carbon bond formation⁷ and halogenation.⁸ This reagent has been reviewed⁹ for reactions involving carbon-nitrogen, carbon-sulfur, carbon-selenium, and carbon-halogen bond formations. In addition, this reagent is used in the one-pot synthesis of various heterocycles including dihydrofurans, tetrahydrofurans and aminotetralins.¹⁰

Abstracts

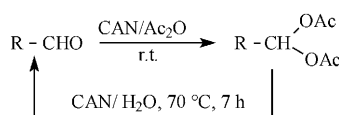
(A) CAN is used as a catalyst for the Michael addition of indole to α,β -unsaturated ketones under ultrasonic irradiation in excellent yields. Substitution takes place at the 3-position, and N-alkylation products are not observed.¹¹



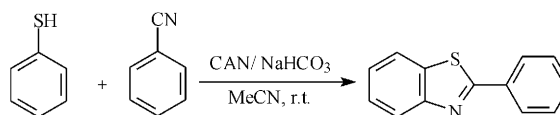
(B) CAN is used as a catalyst for selective esterification of N-Boc protected amino acids. The aliphatic/aromatic amino acids are selectively esterified without affecting the N-Boc protection.¹²



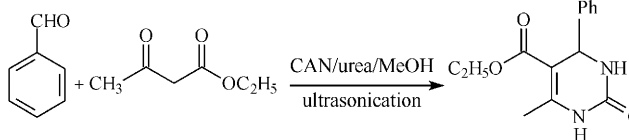
(C) A mild and efficient method has been developed for the chemoselective synthesis of geminal diacetates from aldehydes using acetic anhydride in the presence of a catalytic amount of CAN and ketones are unaffected. Also the deprotection of acylals is carried out by using water and CAN.¹³



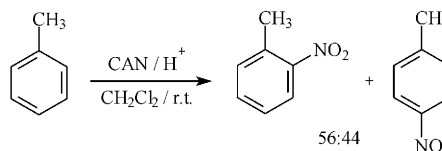
(D) CAN is utilized in a novel synthesis of 2-arylbenzothiazoles by cyclization of the intermediate radical formed after initial oxidative coupling between thiophenols and aromatic nitriles in excellent yield.¹⁴ Also it was used in a one-pot synthesis of isooxazole derivatives from alkynes.¹⁵



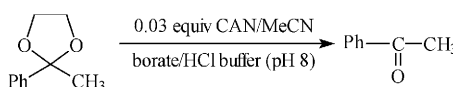
(E) Yadav et al.¹⁶ reported a facile three-component condensation of aldehyde, β -keto ester and urea for the synthesis of 3,4-dihydropyrimidin-2(1H)-one in good yield mediated by CAN in a one-pot reaction.



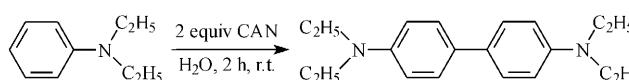
(F) An efficient mononitration of aromatic substrates was developed, using CAN suspended in dichloromethane in the presence of two equivalents of sulfuric acid.¹⁷



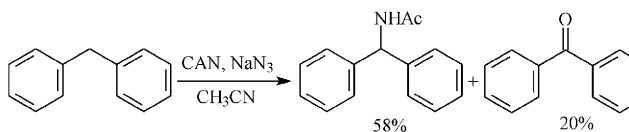
(G) Acetals and ketals are selectively deprotected in good to excellent yields under neutral or mildly basic conditions with a catalytic amount of CAN. The reaction tolerates a range of functional groups including unprotected secondary and tertiary alcohols, ketones, enones and triisopropyl ethers. Also, the aldehyde formed by deprotection is stable under the experimental conditions.¹⁸



(H) In an environmentally benign protocol,¹⁹ oxidative coupling of *N,N*-dialkylarylamines takes place in high yield using CAN as an oxidant in aqueous medium.



(I) In a simple and mechanistically interesting reaction for CH oxidation culminating in Ritter amidation, Nair et al.²⁰ reported a one-pot synthesis of acetamides from unactivated hydrocarbons using CAN in combination with sodium azide in acetonitrile medium.



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