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Recent advances in CAN mediated reactions in organic synthesis

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ABSTRACT

The emergence of CAN as a versatile one-electron oxidant is attested by the wide range of reactions that can be executed by this reagent. The literature on CAN chemistry is updated in the present review while highlighting the reactions that make CAN an exceptional reagent.

1. Introduction

Gomberg's original discovery of triphenylmethyl radical in 1900[1] and the subsequent mechanistic investigations on radical reactions by Hey and Waters[2] and Kharasch[3] set the stage for the use of radical species in organic synthesis. However serious application of radical chemistry especially in carbon–carbon bond formation began only after Stork's seminal work demonstrating that the controlled generation of vinyl radicals and their addition to alkenes constituted a unique and powerful protocol for the construction of complex carbocyclic frameworks.[4–6] Contemporaneous investigations by Julia,[7,8] Beckwith,[9] Ingold et al.,[10] and Giese[11] secured the mechanistic underpinnings of radical chemistry. Subsequent research by many investigators most notably by Hart,[12] Curran,[13,14] Fraser-Reid et al.,[15] and Pattenden et al.[16] made outstanding contributions to the field of radical mediated organic synthesis. Among the various methods known for generation of radicals[17–21] redox processes involving electron transfer deserves special mention.[22] Chemical methods for electron-transfer oxidation generally involve the use of salts of high valent metals such as Mn(III), Cu(II), Ag(I), Co(III), V(V), Fe(III), etc. Most of these species have been employed in C–C bond forming reactions and other synthetic transformations. In this group, $Mn(OAc)_3$ has been the most popular reagent.[23] In spite of its widespread use, poor solubility in organic solvents and the formation of byproducts have limited its utility especially in intermolecular reactions. In view of the drawbacks of the other reagents, the emergence of Ce(IV) reagents as suitable one-electron oxidants assumes importance in this context.

1.1. Cerium (IV) ammonium nitrate (CAN) as a one-electron oxidant

Cerium (IV) ammonium nitrate is known to effect different kinds of oxidative transformations. The versatility of CAN is supported by the fact that there are a large number of research papers and several reviews concerning CAN mediated reactions.[24–34] The unique property that enables cerium to display stable adjacent oxidation states +3 and +4 makes it special among the lanthanide elements. The enhanced stability of the vacant *f* shell in Ce^{+4} accounts for the ability of cerium to exist in the +4 oxidation state Additionally, the large reduction potential value of 1.61 V (vs NHE) endowed in Ce^{+4} makes Ce(IV) reagents superior oxidizing agents compared to other metal ions. The low toxicity, ease of handling, experimental simplicity, and solubility of CAN in a number of organic solvents makes it very valuable. As early as 1965, Trahanovsky and Young showed that benzyl alcohols underwent oxidation to benzaldehydes in excellent yields by using CAN in 50% aqueous acetic acid.[35] Subsequently, the oxidation of toluene to benzaldehyde,[36,37] the oxidation of primary alkanols to tetrahydrofurans,[38] and cleavage of 1,2-diols were all effected using CAN.[39] The pioneering work of Heiba and Dessau in 1971 showed that Ce(IV) reagents are useful for C–C bond forming reactions.[40,41] They have illustrated that electrophilic carbon centered radicals of the type CHX_2 generated by the cerium(IV) oxidation of compounds CH_2X_2, where X is an electron withdrawing group, viz., CO_2R, COR, etc., can be trapped by various alkenes resulting in the formation of different products. Subsequent studies by Baciocchi et al. on the oxidative addition of radicals generated from ketones and 1,3-dicarbonyl compounds to olefins led to the formation of 1,4-diketones[42] and furan derivatives,[43] respectively. The reactions of CAN and related reagents are classified into five categories.

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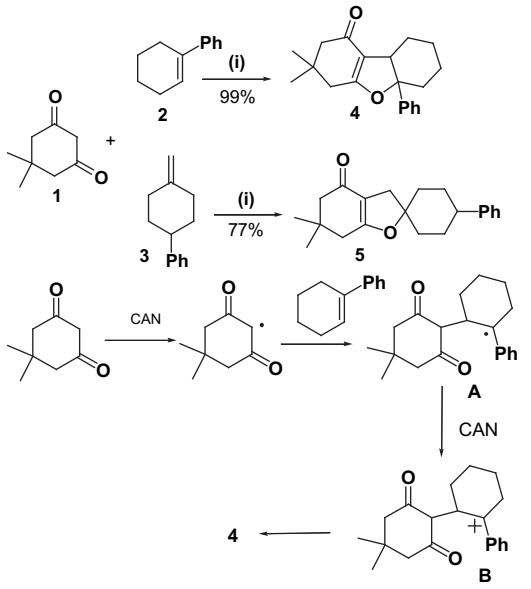
2. Carbon–carbon bond forming reactions

Carbon–carbon bond forming reactions mediated by CAN are broadly divided into two classes: (i) intermolecular reactions and (ii) intramolecular reactions.

2.1. Intermolecular carbon–carbon bond forming reactions

Intermolecular carbon–carbon bond forming reactions mediated by cerium (IV) ammonium nitrate can be classified according to the substrate from which the radical is generated and its mode of addition.

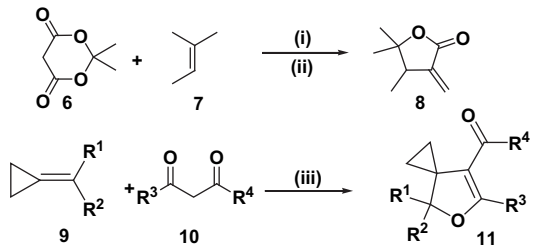
2.1.1. Generation of carbon centered radicals from carbonyl and dicarbonyl compounds. Oxidative addition of radicals generated from ketones and 1,3-dicarbonyl compounds by CAN to olefins may be considered as the most versatile C–C bond forming reaction of CAN and it has been widely utilized for the synthesis of heterocyclic systems. The facile generation of dihydrofuran **4** and spirodihydrofuran **5** by the CAN mediated oxidative addition of dimedone **1** to olefins is illustrated in Scheme 1.[44] It is conceivable that the mechanism of the reaction involves the CAN mediated generation of a radical from dimedone **1**, which is trapped by the alkene giving the intermediate radical species **A**. In the second step the radical **A** is oxidized to cation **B** by the second equivalent of CAN. The latter then undergoes cyclization to afford the dihydrofuran **4**. A similar mechanistic postulate may be invoked for the various reactions involving CAN and carbonyl compounds.



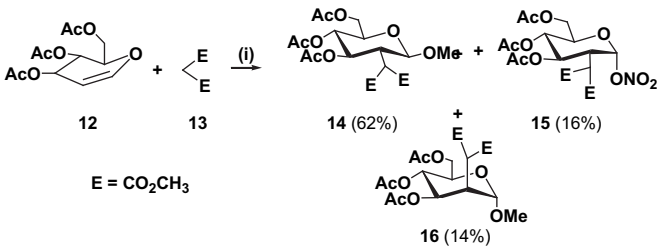
Scheme 1. (i) CAN (2 equiv), MeOH, 5 °C, 15 min.

A two-step procedure for the synthesis of α-methylene lactone **8** by the reaction of alkenes and Meldrum's acid mediated by CAN was developed recently.[45] Spirocyclopropyl dihydrofuran derivative **11** was obtained via the same strategy from methylene cyclopropanes (MCPs) in good yields (Scheme 2).[46]

Malonate radicals formed in the presence of CAN added to styrenes to form lactones via the intermediacy of a benzylic radical and its transformation to a hydroperoxide.[47] Linker has reported the addition of malonates to glycals in the presence of CAN leading to the facile formation of C-2 branched sugars (Scheme 3).[48–50] The remarkable stability of glycals under oxidative conditions was justified by their redox data in solution.[51]

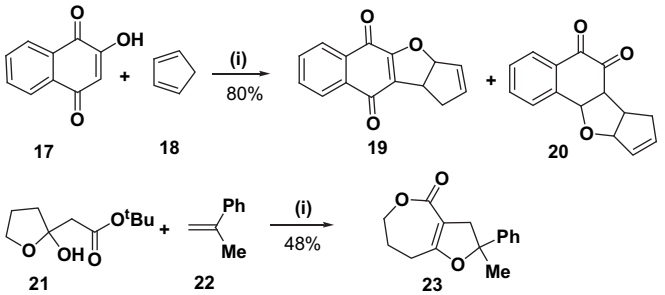


Scheme 2. (i) CAN, MeCN, 0 °C; (ii) Et_2NH, HCHO, NaOAc, HOAc; (iii) CAN, MeOH, Ar, 0 °C, 30 min, R^1=R^2=Ph, R^3=CH_3, R^4=OEt, 77%.



Scheme 3. (i) CAN, MeOH, 0 °C.

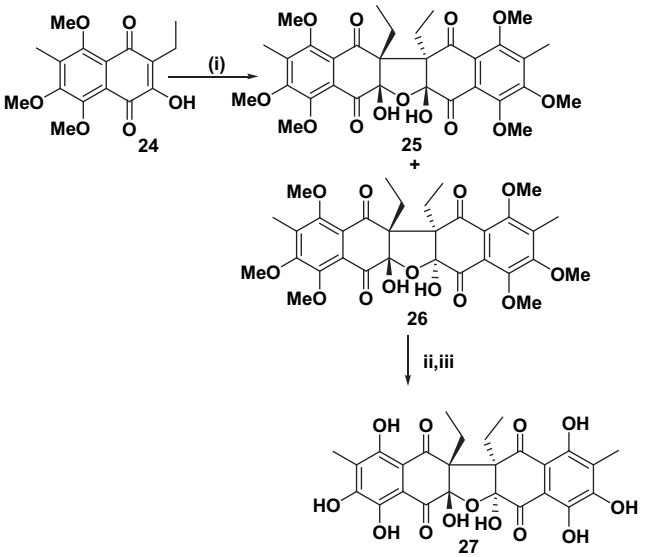
The [3+2] cycloaddition of 2-hydroxy-1,4-naphthoquinone **17** to alkenes mediated by CAN resulted in the formation of furo-*p*-quinones as well as *o*-quinone derivatives.[52] This was further utilized for the synthesis of phenalenofuranones,[53] furopyranones, furoquinolinones,[54] and dihydrofuropyrimidinediones.[55] Synthesis of tetrahydrofuro[3,2,-*c*] oxepin-4(6*H*)-one **23** was achieved by the reaction of 2-(2-hydroxytetrahydrofuran-2-yl)acetate **21** with alkene **22** (Scheme 4).[56]



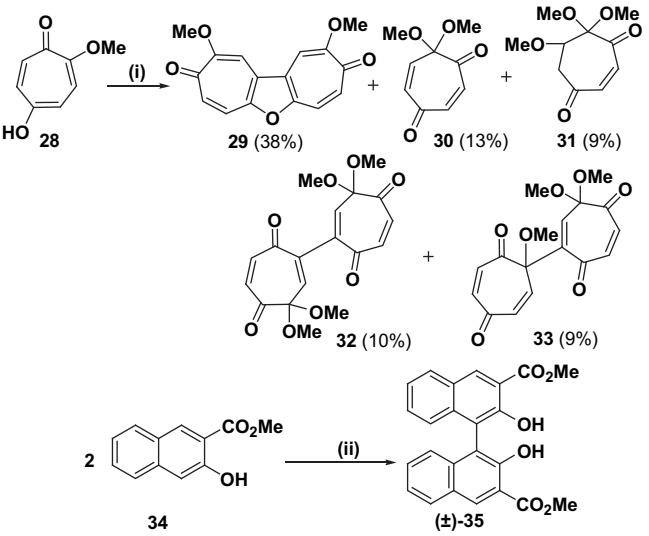
Scheme 4. (i) CAN (2 equiv), MeCN, 0 °C.

2.1.2. Dimerization of carbon centered radicals. Oxidative homocoupling of diethyl malonate to afford tetramethyl ethane-1,1,2,2-tetracarboxylate was effected in the presence of CAN and magnesium oxide.[57] Dimerizations of 4-hydroxyquinolin-2-(1*H*)-ones and 3-alkylated 4-hydroxyquinolin-2-(1*H*)-ones mediated by CAN have also been studied.[58] A remarkable example of CAN mediated dimerization of radicals generated from dicarbonyl compounds is provided by Nicolaou's synthesis of racemic hybocarpone **27**. The key intermediate in the synthesis was obtained by the CAN promoted oxidative dimerization of naphthazarin **24** (Scheme 5).[59]

The CAN promoted oxidation of 5-hydroxy-2-methoxy tropone (**28**)[60] and 4-hydroxy tropone[61] afforded the corresponding dimeric products. Oxidative coupling of 3-carbomethoxy 2-naphthol (**34**) by CAN afforded (±)-binaphthol (**35**)[62] in excellent yields (Scheme 6).



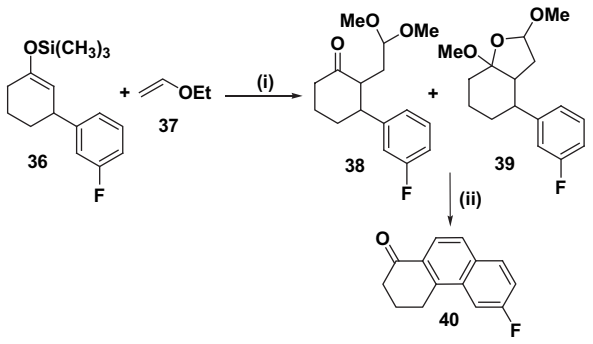
Scheme 5. (i) CAN, degassed MeCN, −35 °C to 0 °C, 3 min, 36%; (ii) AcOH, 10 min, >95%; (iii) $AlBr_3$, EtSH, CH_2Cl_2, 0 °C, 1 h, 60%.



Scheme 6. (i) CAN, MeOH; (ii) CAN, MeOH, rt, 10 min, 94%.

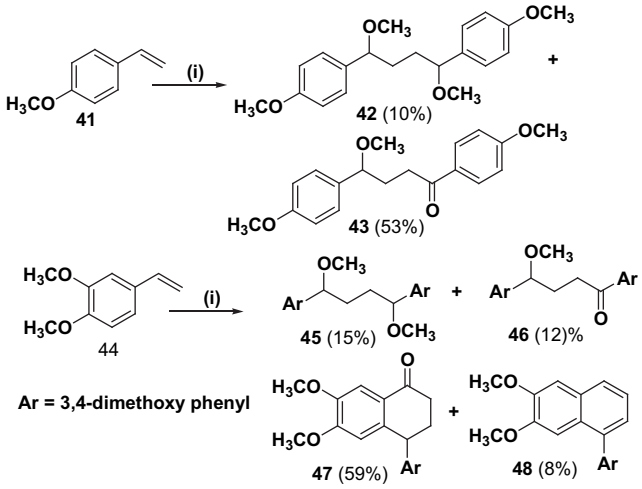
2.1.3. Cross-coupling of electron rich systems via carbon centered radicals. Just as the homocoupling, cross-coupling of electron rich species mediated by CAN also occurs readily. Thus radicals generated from silyl enol ethers, in addition to undergoing self-coupling,[63] have been shown to add to enamines[64a] and dienes[64b] to generate 1,4-dicarbonyl and α,β-unsaturated carbonyl compounds, respectively. A very efficient method for inter- as well as intramolecular C–C bond formation via radical cations derived from metal enolates is known in the literature.[65] Recently, it was also shown that dialkyl silyl bis-enol ether undergoes diastereoselective oxidative coupling in the presence of CAN as the oxidizing agent.[65c] Oxidative addition of 3-aryl-1-(trimethysilyl)oxy cyclohexene **36** to ethyl vinyl ether **37** resulted in the formation of 3,4-dihydro-(2*H*)phenanthrene-1-one **40** as depicted in Scheme 7.[66]

2.1.4. Generation of radical cations from styrenes and related chemistry. CAN has been shown to elicit multiple reactivity profiles in its reaction with styrenes. The reactions were found to be clearly dependent on the substituents at the benzene as well as on the solvent used. For example, 4-methoxy styrene (**41**) underwent facile



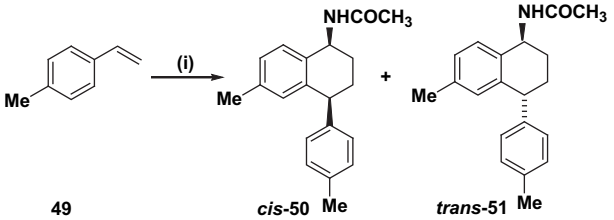
Scheme 7. (i) CAN, MeOH, rt; (ii) 80% aq H_2SO_4, DDQ, 60%.

dimerization to afford **42** and **43** with CAN in methanol.[67] While, styrenes devoid of any alkoxy groups on the benzene ring reacted to afford α-methoxy acetophenones, 3,4-dimethoxy styrene **44** in methanol gave rise to different products **45**–**48** (Scheme 8).[68] The mechanistic details of these reactions are given in our review.[34]



Scheme 8. (i) CAN (2.5 equiv), MeOH, 0 °C, 30 min.

α-Acetamidotetralins *cis*-**50** and *trans*-**51** were obtained in good yields by the reaction of 4-methylstyrene **49** with CAN in acetonitrile (Scheme 9).[69a] α-Aminotetralin derivatives manifest a number of important and therapeutically useful biological activities; some of them are potent CNS stimulants and others are antibiotics, immunomodulators, and antitumor agents.[69b]

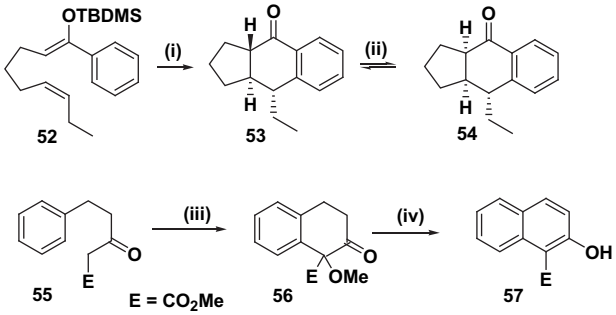


Scheme 9. (i) CAN, dry MeCN, Ar, 2 h, rt, 62% (cis–trans, 1.3:1).

2.2. Intramolecular carbon–carbon bond forming reactions

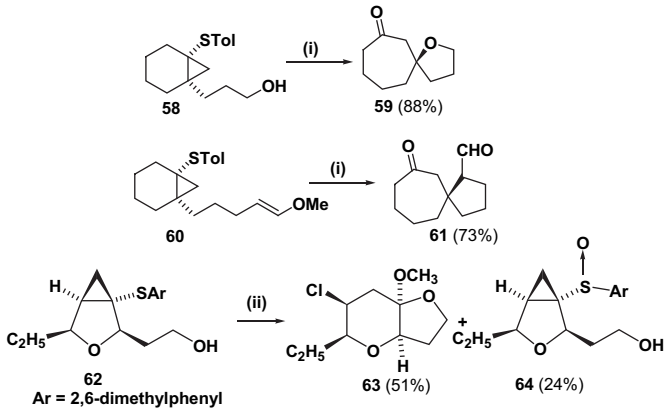
The first report on a Ce(IV) promoted intramolecular reaction involves presumably the inadvertent cyclization of 1-benzyl-2,6-bis-[2′-pyridyl]-4-piperidone-3-carboxylic acid methyl ester mediated by cerium(IV) sulfate in very low yields.[70] There were also reports on the formation of butyrolactones by the oxidative

cyclization of γ-phenyl butanoic acids with CAN in acetonitrile.[71] Oxidative cyclization of δ,ϵ- and ε,φ-unsaturated silyl enolether **52** by CAN leading to tricyclic ketone **54** in high yields and with excellent diastereoselectivity was reported by Snider and Kwon.[72] 2-Hydroxy-1-naphthoic acid esters (and amides) of type **57** were synthesized by the CAN promoted cyclization of 5-aryl-3-oxopentanoic acid ester (or amide) **55** (Scheme 10).[73]



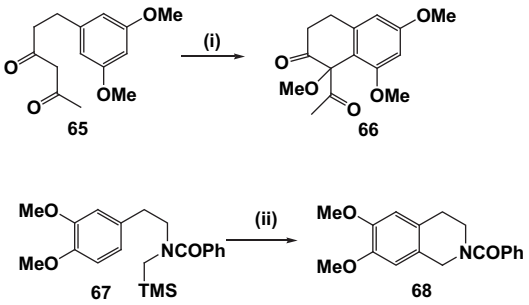
Scheme 10. (i) CAN, $NaHCO_3$, MeCN, 25 °C, 73%, 20:1; (ii) KOH, MeOH; (iii) CAN, CH_3OH, 20 °C; (iv) silica gel, benzene, 62%.

Hydroxyalkyl substituted cyclopropylsulfides underwent single electron-transfer oxidation mediated by CAN affording cyclic ethers and spirocyclic compounds.[74] The reaction is presumably initiated by the formation of thio cation radical followed by ring opening of the cyclopropane and subsequent events to afford the final products.[34] This strategy was used in the asymmetric synthesis of oxaspiro undecanone **59** and cis-fused chlorinated bicyclic ether **63** from optically active bicyclo [4.1.0] heptyl sulfide **58** and cyclopropylsulfides of the type **62**, respectively (Scheme 11).[75,76]



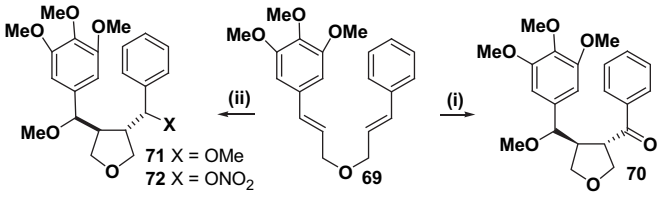
Scheme 11. (i) CAN, aq MeOH, K_2CO_3, 0 °C, 88%; (ii) CAN, NH_4Cl, MS 3 Å, MeOH, rt.

It was reported that 5-*exo* cyclization of tertiary amino cyclopropanes with suitably tethered olefins led to the formation of bicyclic products.[77] CAN mediated 4-*exo-trig* cyclization of α-carbonyl radicals offered an expeditious route to functionalized β-lactams from substituted enamides.[78] Recently, the ability of CAN to fragment the cyclopropyl moiety was utilized in the synthesis of benzotropolones by Hasegawa et al.[79] Efficient CAN mediated intramolecular cyclizations onto the benzene ring have been reported. The reactions of δ-aryl-β-dicarbonyl compound **65** and phenethylamide **67** leading to β-tetralones **66** and dihydroisoquinoline **68**, respectively, are illustrative examples (Scheme 12).[80,81]



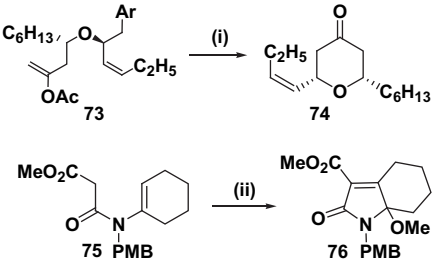
Scheme 12. (i) CAN, MeOH, 60% (ii) CAN, dry MeCN, 8 h, 60%.

Stereoselective formation of trans-3,4-disubstituted tetrahydrofuran derivative **70** was effected by the CAN mediated reaction of the corresponding dicinnamyl ether **69** in moderate yields. Under argon atmosphere, the reaction afforded the corresponding tetrahydrofuran derivatives as a mixture of methoxy and nitrato derivatives **71** and **72** in 2:1 ratio in high yields (Scheme 13).[82]



Scheme 13. (i) CAN, MeOH, 0 °C, oxygen, 0.5 h, 56%; (ii) CAN (2.3 equiv), MeOH, rt, Ar, 90 min 87%.

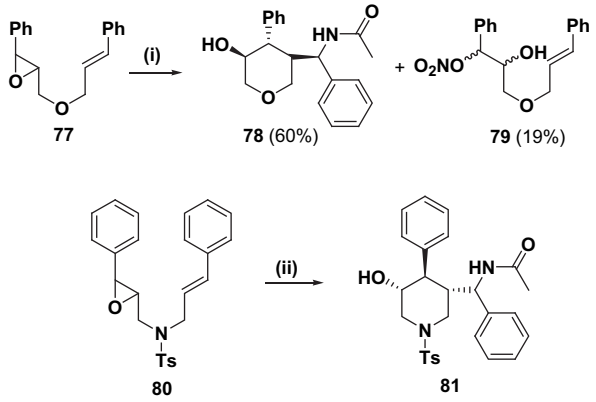
It has been shown that homobenzylic ethers with pendant enolacetate moiety such as **73** can undergo highly efficient cleavage followed by 6-*endo* cyclization in the presence of CAN to afford tetrahydropyrone **74** with excellent stereocontrol.[83] 5-*endo* Cyclization of enamide esters such as **75** in the presence of CAN led to disubstituted γ-lactam **76** in moderate yields.[84] In this paper, the authors suggest that the radical generated from **75** undergoes a 5-*endo* cyclization and subsequent oxidation to an acyl iminium ion. The latter then undergoes elimination followed by a radical generation and oxidation sequence to furnish a second iminium ion intermediate, which upon trapping with the solvent furnishes the observed product **76**. This method has been used to synthesize the heterocyclic ring fragments of the natural products L-755,807, quinolacticin C, and PI-091 (Scheme 14).



Scheme 14. (i) CAN (4 equiv), MeOH, rt, 65%; (ii) CAN (4 equiv), $NaHCO_3$, 4 Å MS, MeCN, DCE.

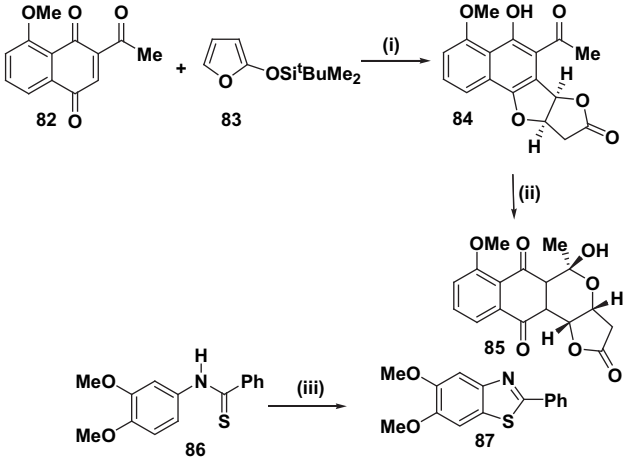
Catalytic amounts of CAN were used for the cyclization of epoxy cinnamyl ethers leading to the synthesis of 3,4,5-trisubstituted tetrahydropyran derivatives in good yields.[85] It is noteworthy that the compound **78** was obtained stereoselectively; it has four contiguous stereocenters and has some resemblance to the naturally occurring bioactive norlignans called sequirins. The reaction presumably involves the formation of the radical cation on oxygen

followed by ring opening of the epoxide in an intramolecular fashion and subsequent events to afford the final product. On similar grounds, the stereoselective intramolecular cyclization of epoxy cinnamyl amines mediated by CAN led to the synthesis of functionalized piperidine **81** (Scheme 15).[86] The intramolecular cyclization of *N*-cinnamyl *N*-tosyl-2-methoxycinnamyl amines and α-cinnamyl-α-(2-methoxycinnamyl)-malonates led to the synthesis of trans-3,4-disubstituted pyrrolidines and cyclopentanes, respectively.[87]



Scheme 15. (i) CAN (0.5 equiv), MeCN, Ar, 16 h; (ii) CAN (0.8 equiv), MeCN, Ar, 5 h, 62%.

The CAN mediated intramolecular cyclization strategy was used by Brimble et al.[88] for the synthesis of several pyranonaphthoquinone antibiotics, the key step being the oxidative cyclization of furonaphthofuran adducts such as **84**. The product **85** was formed by the oxidative cyclization of the furonaphthofuran adduct **84**, which in turn was formed by the conjugate addition of dimethyl *tert*-butyl silyloxyfuran **83** to the 1,4-quinone **82**. Recently intramolecular cyclization of thiobenzamide **86** to benzothiazole **87** via aryl radical cations generated by CAN was reported (Scheme 16).[89] The reaction involves the formation of the thiol radical cation along with the aryl radical cation. Cyclization of the latter yields the benzothiazole while the former on reaction with water affords benzamide as a byproduct.



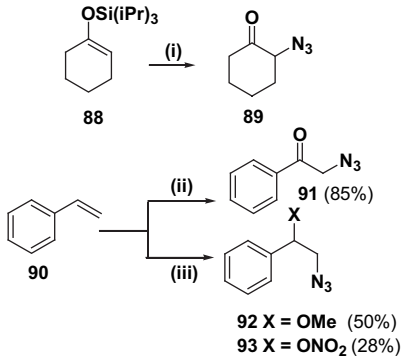
Scheme 16. (i) $BF_3{\cdot}OEt_2$, CH_2Cl_2, −78 °C, 1 h, 45%; (ii) CAN (2 equiv), MeCN–H_2O (1:1), 21%; (iii) CAN (1.1 equiv), MeCN–H_2O, rt, 30 min, 94%.

3. Reactions involving carbon–heteroatom bond formation

Heteroatom centered radicals formed by the oxidation of anions by CAN undergo efficient addition to alkenes or alkynes leading to the formation of a variety of interesting products.

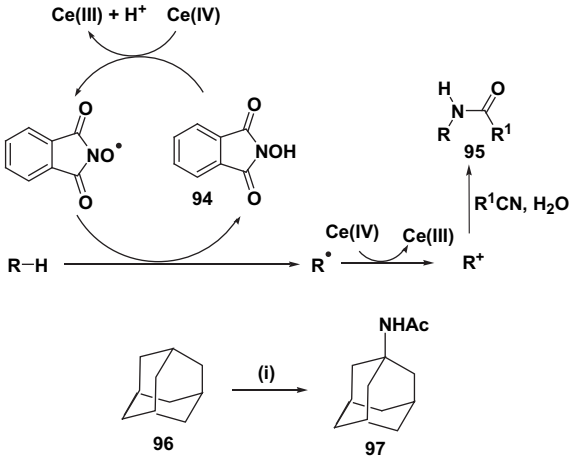
3.1. Carbon–nitrogen bond formation

3.1.1. Introduction of azide functionality. As early as 1971, Trahanovsky reported the first example of azidonitration mediated by CAN.[90] Subsequently, this protocol was used to synthesize azidosugars[91] and amino acids.[92] The oxidative azidation of silyl enol ethers leading to the formation of α-azidoketones was first reported by Vogel and Auberson.[93] Subsequently, the reaction was studied in detail employing triisopropyl silyl enol ether such as **88** as the substrate in acetonitrile as solvent.[94] The reaction of styrene with CAN and sodium azide in methanol in oxygen atmosphere led to the formation of α-azidoketone **91** whereas argon atmosphere afforded the azidomethyl ether **92** (Scheme 17).[95] Mechanistically, the azido radical formed by the oxidation of the azide anion by CAN adds to styrene yielding the benzylic radical, which is subsequently quenched by molecular oxygen to form **91**. The β-methoxy and β-nitrato products can result from the quenching of the benzylic cation by methanol and nitrate, respectively.



Scheme 17. (i) CAN, NaN_3, MeCN, −20 °C, Ar, 72%; (ii) NaN_3, CAN, MeOH, O_2, 0 °C; (iii) NaN_3, CAN, MeOH, Ar, 0 °C.

3.1.2. Introduction of nitro and amido functionalities. There are many reports on the efficient nitration potential of CAN.[96–100] Ritter type reaction of alkyl benzene with nitrile was reported using *N*-hydroxy-phthalimide (NHPI) **94** and CAN.[101] Subsequent work has shown that CAN in combination with sodium azide can react with unactivated hydrocarbons such as adamantane **96** in acetonitrile to furnish acetamide **97** in good yields (Scheme 18).[102] The reaction was found to be applicable for the C–H activation of a variety of substrates.

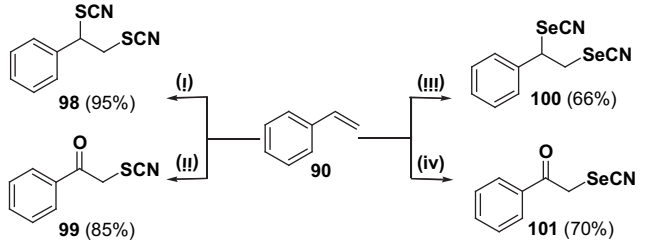


Scheme 18. (i) CAN (2.3 equiv), NaN_3, MeCN, Ar, rt, 30 min, 85%.

Apart from these, CAN is also known to nitrate aromatic compounds efficiently to produce mono as well as dinitro derivatives.[103–110]

3.2. Carbon–sulfur and carbon–selenium bond formation

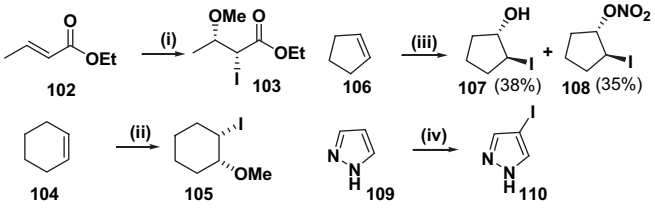
It has been reported that sulfinates undergo CAN mediated oxidative addition to styrenes yielding keto and nitrato sulfinates.[111] Thiocyanation and selenocyanation of styrenes afforded different products depending on the reaction conditions employed. In deoxygenated solutions at ice-cold conditions dithiocyanate **98** (or diselenocyanate **100**) was formed in excellent yield, whereas in an atmosphere saturated with oxygen, phenacyl thiocyanate **99** (or phenacyl selenocyanate **101**) was the predominant product (Scheme 19).[112–114] The same combination of reagents effected the thiocyanation of indoles, pyrroles, and thiophenes.[115]



Scheme 19. (i) NH_4SCN, CAN, MeOH, rt, 15 min; (ii) NH_4SCN, CAN, 0 °C, MeOH, O_2, 30 min; (iii) KSeCN, CAN, MeOH, Ar, 0 °C; (iv) KSeCN, CAN, MeOH, O_2, 45 min.

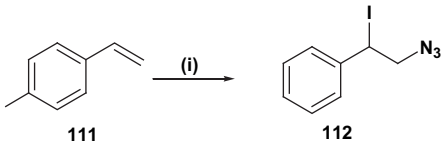
3.3. Carbon–halogen bond formation

3.3.1. Bromination and iodination. Bromination of alkenes to afford vicinal dibromides was effected by using potassium bromide and CAN in a two-phase system of water and dichloromethane; in solvents, such as methanol or acetonitrile, phenacyl bromide and 1,2-nitrato bromide were formed.[116] Efficient CAN mediated bromination and iodination at C-5 of uracil nucleosides has been achieved using catalytic amounts of CAN and potassium bromide in acetonitrile or DMF.[117] A stereoselective synthesis of 2-deoxy-2-iodo-α-*manno*-pyranosyl acetate by the CAN mediated addition of iodide to glycals has been reported recently by Roush et al.[118] Iodination of α,β-unsaturated ketones and esters with iodine and CAN in methanol under reflux conditions afforded the corresponding β-methoxy α-iodoketones and esters in good yields [119] while in acetonitrile, β-hydroxy α-iodoketones and esters were obtained. Similarly, cycloalkenes on treatment with iodine and CAN in methanol under reflux conditions gave the corresponding vicinal alkoxyiodo cycloalkanes,[120,121] while in *tert*-butanol, the product formed was *trans*-1,2-iodonitrate. When the solvent system was acetonitrile–water the corresponding *trans*-iodohydrins and *trans*-iodonitrates resulted.[122] The regioselective iodination of pyrazoles using elemental iodine and CAN constitutes a mild and efficient method for the preparation of 4-iodopyrazoles.[123] Scheme 20 depicts some typical iodination reactions mediated by CAN.



Scheme 20. (i) CAN, MeOH, 52%; (ii) CAN, MeOH, 92%; (iii) CAN, I_2, CH_3COOH, H_2O; (iv) CAN, I_2, MeCN, 98%.

3.3.2. Azido-iodination and iodo-thiocyanation. CAN mediated double functionalization of alkenes using NaI and NaN_3 has been shown to be a convenient protocol for the synthesis of azidoiodides (Scheme 21).[124] The reaction is applicable to a variety of alkenes. For instance, styrenes on treatment with ammonium thiocyanate and sodium iodide in the presence of CAN led to the formation of iodothiocyanate and phenacyl thiocyanate. With cyclohexene and octene, the corresponding iodothiocyanate was the only product.

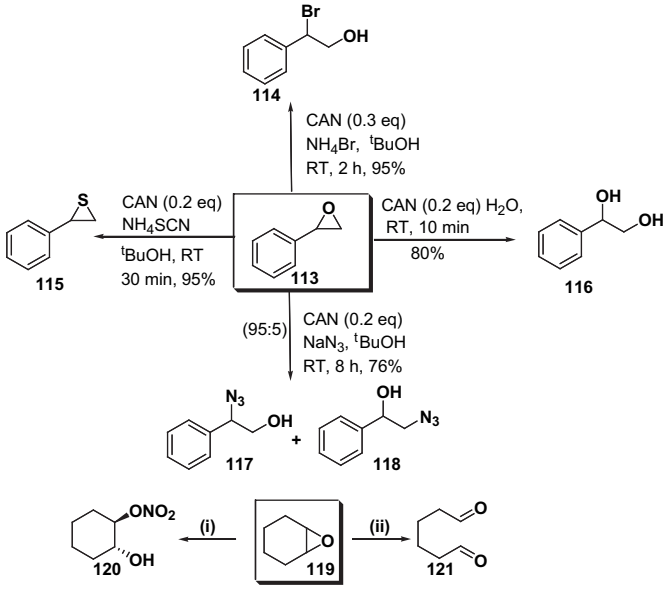


Scheme 21. (i) NaN_3, NaI, CAN, MeOH, 0 °C, 30 min, 71%.

4. Reactions involving CAN as a catalytic oxidant

4.1. Oxidative transformations of epoxides

Regioselective ring opening of epoxides[125] and cleavage of epoxides to dicarbonyl compounds[126] under the influence of CAN have been reported. Conversion of epoxides to β-nitrato alcohols has been utilized in the preparation of key intermediates in the synthesis of novel tricyclic β-lactam derivatives endowed with outstanding chemical and metabolic activity.[127] Analogous to the ring opening reactions of epoxides, cleavage of *N*-tosyl aziridines to afford amino alcohols has been reported.[128] The various transformations of CAN mentioned above are summarized in Scheme 22 taking styrene epoxide as a representative substrate. Recently, the regioselective formation of *syn*-β-bromo-α-hydroxy ketones was reported by the ring opening reaction of the epoxide obtained from benzal acetophenone but the reaction utilized stoichiometric amounts of CAN.[129]



Scheme 22. (i) CAN (0.2 equiv), NH_4NO_3, aq MeCN, rt, 15 min, 80%; (ii) CAN (0.2 equiv), aq MeCN, rt, 1 h, 60%.

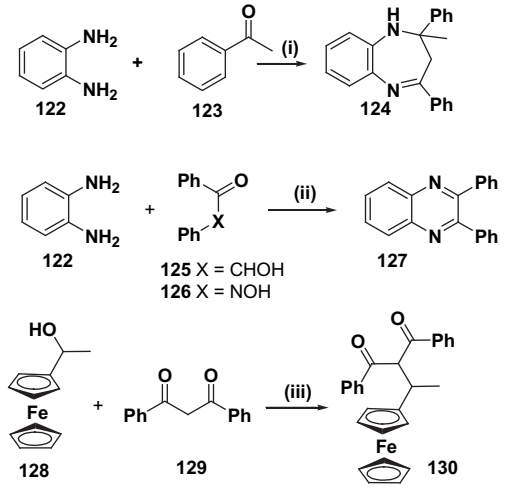
4.2. CAN-bromate oxidations

The catalytic role of CAN in oxidations with bromate ion serving as the co-oxidant has been investigated. Oxidation of benzyl alcohol to benzaldehyde in the presence of CAN and sodium bromate is the first report on this type of reaction.[130] The oxidation of alkyl aromatic compounds to ketones with CAN and potassium bromate was reported later.[131] The oxidative cleavage of alkyl ethers and trialkyl silyl ethers was reported with CAN and sodium bromate.[132] The selective oxidation of secondary alcohols in the presence of

primary alcohols was also effected with the CAN-bromate reagent combination.[133] It is also noteworthy that CAN in catalytic amounts has been shown to facilitate the hydrolysis of peptides.[134]

4.3. Other transformations catalyzed by CAN

CAN was shown to be an effective catalyst for the electrophilic substitution reaction of indoles with carbonyl compounds resulting in the formation of di- and tri-indolylmethanes in high yields.[135] The reaction of *o*-phenylenediamine and ketones leading to the synthesis of 1,5-benzodiazepine derivative **124** was also found to be catalyzed by CAN.[136] The direct conversion of α-hydroxy ketones and α-keto oximes into quinoxaline derivatives **127** in the presence of a catalytic amount of CAN, via metal-catalyzed aerobic oxidation of **126** followed by in situ trapping with aromatic 1,2-diamines, in water was reported.[137] A catalytic amount of CAN was also used for the substitution reaction of ferrocenyl alcohol **128** with various nucleophiles thus providing an easy access to functionalized ferrocenes (Scheme 23).[138]

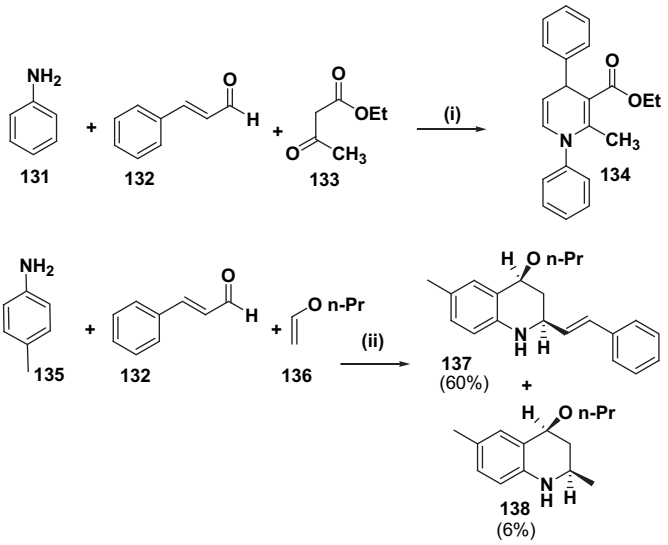


Scheme 23. (i) CAN (10 mol %), MeOH, rt, 3.5 h, 89%; (ii) CAN, air–H_2O, rt, 50 min, X=CHOH (97%), X=NOH (72%); (iii) 5 mol % CAN, MeCN, 98%.

Recently, it was reported that CAN catalyzes the three-component domino reaction between aromatic amines, α,β-unsaturated aldehydes, and ethyl acetoacetate, providing an efficient entry into 1,4-dihydropyridines.[139] Similarly a vinylogous version of the Povarov reaction was accomplished by the CAN catalyzed reaction between aniline, cinnamaldehyde, and vinyl ethers resulting in the formation of 2-styryl-1,2,3,4-tetrahydroquinolines.[140] The latter reaction was highly stereoselective yielding the diastereomer with a cis relation between the styryl and alkoxy groups in major amounts. The two reactions above were studied using radical traps and the consistent results suggest that the Lewis acidity of CAN is operating here rather than the latter serving as a single electron oxidant. Representative examples of these reactions are given in Scheme 24.

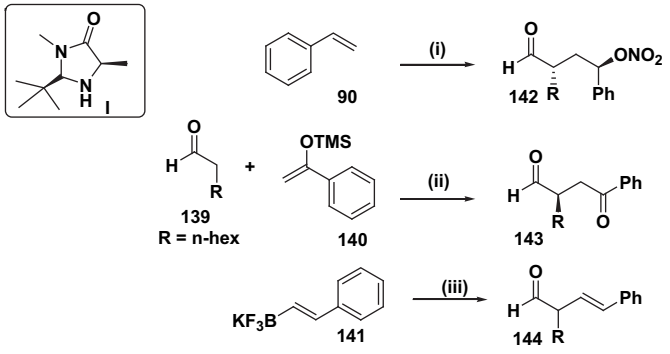
4.4. CAN as a single electron oxidant in organocatalysis

A new route to organocatalytic activation termed as SOMO catalysis was introduced very recently by MacMillan et al.[141] This new strategy is based on the mechanistic hypothesis that the single electron oxidation of a transient enamine intermediate (derived from an aldehyde and an enantiopure amine) will render a 3π electron SOMO activated species that can readily participate in



Scheme 24. (i) 5 mol % of CAN, EtOH, rt, 1 h, 74%; (ii) 15 mol % of CAN, MeCN, 5 h, 60%.

a range of unique asymmetric bond constructions. CAN was used as the stoichiometric oxidant, which can create the transient radical species from the enamine intermediate. Representative examples for the use of this strategy include the carbo-oxidation of styrenes,[142] enantioselective α-enolation,[143] and vinylation[144] of aldehydes. All these reactions are depicted in Scheme 25. The reactions use 20 mol % of chiral imidazolidinone organocatalyst **I** and 2.5 equiv of CAN as stoichiometric catalyst in a water–solvent mixture in the presence of sodium bicarbonate. Extending the methodology, enantioselective intermolecular α-alkylation of aldehydes has been accomplished by using a combined activation pathway involving photoredox catalysis and imidazolidinone based organocatalysis.[145]



Scheme 25. (i) 20 mol % of **I**, 2.5 equiv of CAN, DME–H_2O, $NaHCO_3$, −40 °C, 91%, 96% ee; (ii) 20 mol % of **I**, 2 equiv of CAN, DME, DTPB, −20 °C, 24 h, 83%, 90% ee; (iii) 20 mol % of I, 2.5 equiv of CAN, DME–H_2O, $NaHCO_3$, −50 °C, 24 h, 81%, 94% ee.

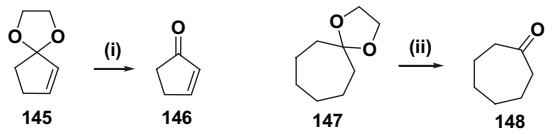
5. Deprotection–protection sequences mediated by CAN

In recent years CAN has emerged as a very efficient reagent for several protection–deprotection reactions.

5.1. Deprotection of acetals

CAN acts as a mild reagent to deprotect the acetal moiety. Nair et al. employed 1.2 equiv of CAN in aqueous methanol (Scheme 26).[146] Simultaneously, Marko et al. also developed two CAN mediated procedures for the deprotection of acetals. Initially they

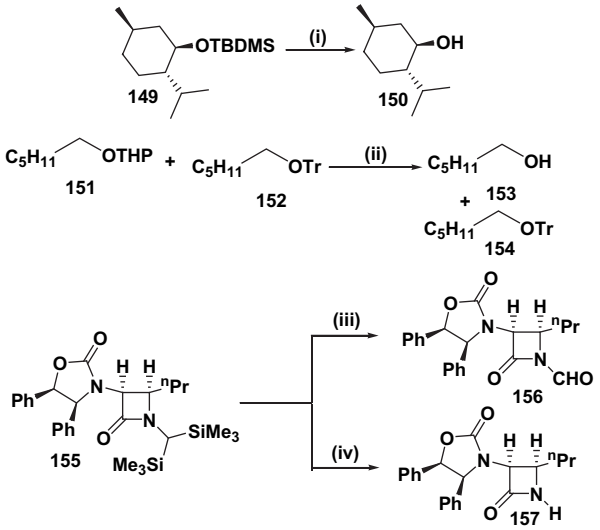
employed 2.5 equiv of CAN in aqueous acetonitrile for the deprotection and demonstrated that the reaction is not an acid catalyzed process, as the deprotection was achieved under basic conditions in the presence of K_2CO_3 as well.[147]



Scheme 26. (i) CAN (1.2 equiv), aq MeOH, rt, 10 min, 80%; (ii) CAN (1.2 equiv), aq MeOH, rt, 10 min, 90%.

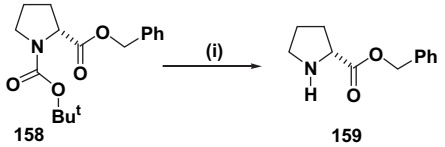
5.2. Removal of TBDMS, THP, and *t*-Boc groups

Singh et al. have reported an efficient procedure for the cleavage of TBDMS ethers using CAN in methanol.[148] Marko et al. also described a CAN catalyzed protocol for the removal of THP ethers under neutral conditions employing 3 mol % of CAN in aqueous acetonitrile and borate buffer (pH 8). Good selectivity was observed in the presence of other protecting groups, which allowed the selective deprotection of a THP group in the presence of a trityloxy substituent (Scheme 27).[149] The ability of CAN to cleave the C–Si bond was utilized for the removal of the *N*-[bis(trimethylsilyl)methyl] moiety from the β-lactam **155**.[150]



Scheme 27. (i) 3 mol % of CAN, MeCN–borate buffer, 2.5 h, 95%; (ii) 3 mol % of CAN, MeCN, borate buffer (pH 8), 60 °C; (iii) CAN (5 equiv), MeOH, rt, 3 h, 89%; (iv) CAN (5 equiv), MeOH, rt, 24 h, 75%.

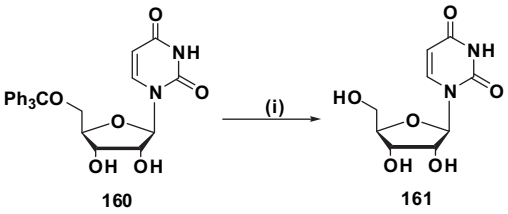
Removal of *t*-Boc group from organic compounds under neutral conditions was effected using catalytic amounts of CAN in acetonitrile.[151] An illustrative example is given in Scheme 28.



Scheme 28. (i) CAN (cat.), MeCN, reflux, 2 h, 93%.

5.3. Removal of trityl group

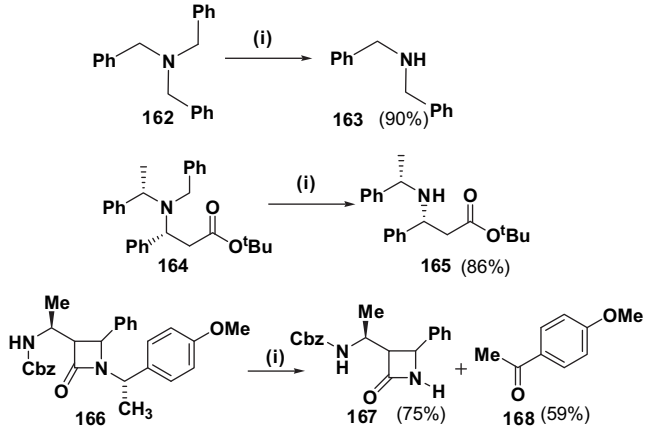
Removal of trityl and monomethoxytrityl groups from protected nucleosides or nucleotides was accomplished by using catalytic amounts of CAN in wet acetonitrile–DMF under neutral conditions (Scheme 29).[152] Deprotection was achieved much faster via electron-transfer processes[153–156] by adsorbing the organic compounds containing the trityl or silyl groups on a CAN–SiO_2 reagent. The same strategy was employed for the selective cleavage of trityl, monomethoxytrityl (MMTr), and dimethoxytrityl (DMTr) groups from protected nucleotides and nucleosides under mild conditions.[157]



Scheme 29. (i) CAN–silica gel, CH_2Cl_2, 25 °C, 80%.

5.4. Removal of benzyl, PMB, and PMPE groups

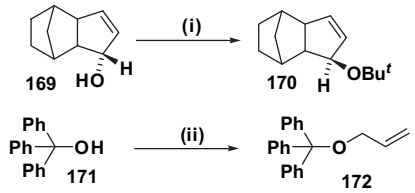
Debenzylation of tertiary amines such as **162** with aqueous CAN afforded the corresponding secondary amines (Scheme 30).[158,159] The strategy was employed for the solid phase synthesis of secondary amines. CAN was also used in the selective cleavage of the PMB (*p*-methoxy benzyl) group in the presence of the NAP (2-naphthylmethyl) group from a range of protected monosaccharides.[160] A new route for the synthesis of oxazolidinone was reported by the CAN mediated debenzylation of *N*,*N*-dibenzylaminoepoxide.[161] The easy removal of the *p*-methoxyphenylethyl (PMPE) group by CAN was used in the synthesis of β-amino acid derivatives.[162] Removal of PMPE group from β-lactam **166** was achieved by using CAN in acetonitrile.[163] Tomioka et al. have reported a CAN mediated oxidative removal of N-PMP (*p*-methoxy phenyl) group.[164]



Scheme 30. (i) CAN (2.1 equiv) MeCN–H_2O (5:1).

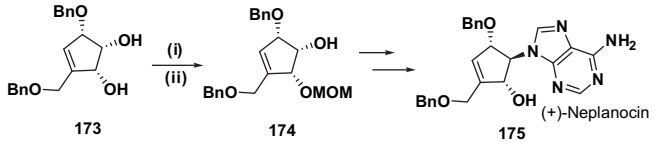
5.5. Protection sequences mediated by CAN

Conversion of allylic and tertiary benzylic alcohols **169** and **171** into the corresponding ethers **170** and **172** was achieved using catalytic amounts of CAN in appropriate alcohols (Scheme 31).[165]



Scheme 31. (i) CAN (0.2 mol %), *t*-BuOH, rt, 24 h, 80%; (ii) CAN (0.2 mol %), allyl alcohol, acetone, reflux, 2 h, 67%.

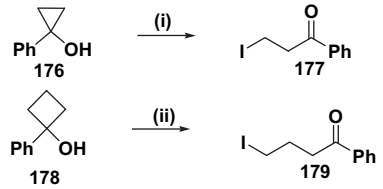
Carbohydrate acetonation using 2,2-dimethoxypropane took place with CAN in anhydrous DMF.[166] Tetrahydropyranylation of alcohols and synthesis of 2-deoxy-*O*-glycosides, catalyzed by CAN, were reported by Vankar and Pachamuthu.[167] An easy route for the preparation of dialkyl and diallyl acetals of aromatic aldehydes mediated by CAN was reported using the corresponding alcohols as the solvent.[168] Rodriguez et al. developed a mono protection reaction of the glycol moiety as in **173** in the presence of catalytic amounts of CAN (Scheme 32).[169] A chemoselective solvent free method for the synthesis of acylals and their deprotection to 4-oxo-4*H*-1-benzopyran-3-carbaldehyde catalyzed by CAN was reported.[170]



Scheme 32. (i) $(MeO)_3CH$, CAN, DCM, 2 h, rt; (ii) DIBAL, −78 °C, 1 h, 0 °C, 10 min, 66%.

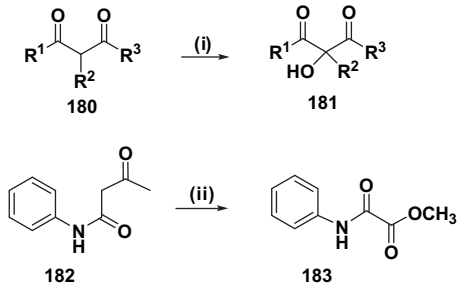
6. Miscellaneous transformations

CAN is known to promote several other reactions, which do not easily fit into the above categories. These include fragmentation, alkoxylation, side-chain oxidation, esterification, transesterification, and dehydrogenation reactions, the details of which can be obtained from our earlier review.[34] CAN mediated ring opening reactions of mono phenyl and diphenyl substituted cyclopropanes in acetic acid and acetonitrile have been studied.[171] The crucial intermediate in a prostaglandin total synthesis, a hydroxyaldehyde lactone is obtained by the CAN catalyzed chromic acid oxidation of a cyclopropanol in aqueous acetic acid.[172] A detailed investigation of the cation radicals of various aryl cyclopropanes generated by CAN has been reported.[173] Recently, Flowers et al. have shown that the selective oxidation of an inorganic anion in the presence of 1-substituted cyclopropanol and 1-substituted cyclobutanol led to the formation of β- and γ-substituted ketones, respectively (Scheme 33). [174,175] The formation of β-substituted ketones was achieved using anions like SCN(−), N_3(−) and halide while γ-substituted ketones were obtained using halide ion.[175] The inorganic radical generated from the anion added to cyclopropanol leading to a radical intermediate, which on subsequent oxidation followed by deprotonation afforded the final product.



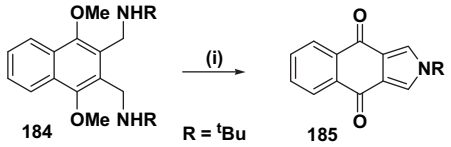
Scheme 33. (i) NaI, 2 equiv of CAN, MeCN–H_2O (80:20), 90%; (ii) NaI, 2 equiv of CAN, DME–H_2O (80:20), 79%.

Dialkyl malonates on treatment with CAN in methanol led to the direct synthesis of tartronic acid derivatives.[176] α-Hydroxylation reaction of β-dicarbonyl compounds with molecular oxygen was studied extensively by Christoffers and occurs via Ce(IV) catalysis.[177] The role of the dioxygen is to oxidize the Ce(III) species to Ce(IV). Oxamates were obtained in good yields by the reaction of acetoacetanilide **182** with CAN in methanol, instead of the expected oxindole. Substantial enhancement of the overall yield was attained when the reaction was performed in an atmosphere of oxygen (Scheme 34).[178]



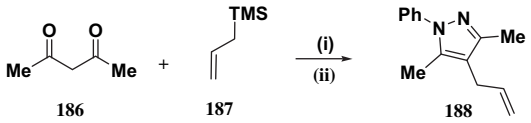
Scheme 34. (i) O_2 (1 atm), cat. $CeCl_3 \cdot 7H_2O$, *i*-PrOH, 23 °C, 16 h; (ii) CAN, O_2, rt, MeOH, 70%.

Oxidation of aminomethyl moieties to the corresponding aldehydes by CAN was used recently in the targeted synthesis of benzo[*f*]isoindole-4,9-diones from 2,3-bis(aminomethyl)-1,4-dimethoxy naphthalenes (Scheme 35).[179]



Scheme 35. (i) 4 equiv of CAN, MeCN–H_2O, 0 °C, 3 h, 87%.

Very recently, a one-pot synthesis of tetrasubstituted pyrazole by the reaction of 1,3-diketone with CAN and allyltrimethylsilane with CAN followed by addition of substituted hydrazine was reported by Flowers et al. (Scheme 36).[180]



Scheme 36. (i) 2.1 equiv of CAN, MeCN, rt, 45 min; (ii) $PhNHNH_2$, 3 mol % of CAN, MeCN, reflux, 3 h.

6.1. Polymerization reactions

CAN has been used as an initiator for co-polymerization reactions. Modification of biopolymers, such as starch, cellulose, guargum, etc. was done using CAN as the initiator.[181] The initially formed co-ordination complex between CAN and the biopolymer underwent disproportionation to form the free radical on the biopolymer chain and Ce(III). A detailed account of such reactions is beyond the scope of this report.[182–186]

7. Conclusions

In conclusion, it is evident from the above discussion that CAN is an exceptionally efficient and versatile reagent for single electron oxidation. The broad range of reactions mediated by CAN is unique

amongst oxidants. Although there have been attempts to use CAN as a catalyst for several organic transformations, this is an area that holds enormous untapped potential. Another area of CAN chemistry that is worthy of exploration is its use in asymmetric synthesis.

Acknowledgements

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