Cerium(IV) Ammonium Nitrate—A Versatile Single-Electron Oxidant

Vijay Nair* and Ani Deepthi

Organic Chemistry Section, Regional Research Laboratory (CSIR), Trivandrum, India

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Contents

* To whom correspondence should be addressed. Phone: 91-471-2490 406. Fax: 91-471 2491712. E-mail: vijaynair_2001@yahoo.com.

1. Introduction

Carbon−carbon and carbon−heteroatom bond-forming reactions constitute the central theme of organic synthesis, and progress in modern synthesis is dependent on development of novel methodologies for the same. Among the various methods for bond formation, single-electron transfer (SET) reactions undoubtedly occupy a prime position. Of the different methods of SET, chemical methods for the generation of radicals have emerged to be very important in recent years. Radicals have been known to the organic chemists ever since the epoch-making discovery of the triphenylmethyl radical by Gomberg in the year 1900.[1,2] Almost four decades later, significant contributions to the development of this area were made by Hey and Waters[3] and Kharasch,[4] who carried out elaborate studies on the mechanisms of radical reactions. In spite of a clear understanding of the mechanistic background, radical reactions found little application in synthesis, largely due to the erroneous notion that they are prone to give intractable mixtures. A dramatic change in this outlook which triggered an upsurge of interest in this approach, particularly over the last three decades, can be attributed to the conceptualization and demonstration by Stork that the controlled generation and addition of vinyl radicals to olefins constitutes a unique and powerful method for complex carbocyclic construction.[5−7] It is noteworthy that the investigations of Julia,[8,9] Beckwith,[10] Ingold,[11] and Giese[12] have contributed to a deeper understanding of the structure and reactivity of radicals. A number of others, most notably, Curran,[13,14] Pattenden,[15] Fraser-Reid,[16] and Hart,[17] have made significant contributions to the application of radical methodology in organic synthesis. Today, radical methodology has evolved as a prominent tool in the arsenal of the synthetic organic chemist.[18,21]

Various procedures involving chemical,[19−21] electrochemical,[22] and photochemical[23] methods are known for generation of radicals. Of these, redox processes based on electron transfer deserve special mention.[24] Chemical methods for

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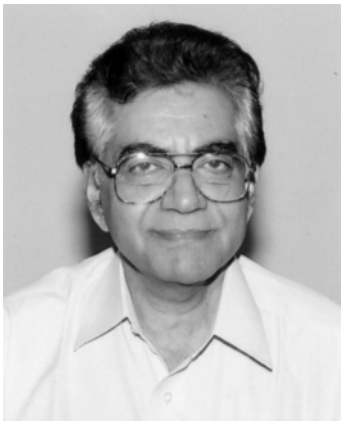


Vijay Nair was born in Konni, Kerala State, India. He has Ph.D. degrees from Banaras Hindu University (1967, with Professor R. H. Sahasrabudhey) and the University of British Columbia (1969, with Professor James P. Kutney). Subsequently, he did postdoctoral work with Professor Josef Fried at the University of Chicago, Professor Peter Yates at the University of Toronto, and Professor Gilbert Stork at Columbia University. He joined the Medical Research Division (Lederle Laboratories) of American Cyanamid Company as Senior Research Chemist in 1974 and became Principal Research Chemist in 1987. In 1981 he received the Outstanding Scientist Award of Cyanamid Company. In 1990, he returned to India to join the Regional Research Laboratory (CSIR) in Trivandrum. From 1997 to 2001 he was the director of the laboratory. He is now continuing in RRL as a Senior Associate of the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore. He is also an Honorary Professor in the Cochin University of Science and Technology. He has lectured in a number of universities in Germany in 1998 under the INSA-DFG exchange fellowship. He has been an invited speaker at the 17th International Conference on Heterocyclic Chemistry in Vienna in 1999, MCR 2000, International Symposium in Munich, and IUPAC-International conference on Organic Synthesis (ICOS-15), Nagoya, Japan, 2004. He was a visiting scientist at Columbia University during 1979–82 and Visiting professor at the University of Pernambuco in Brazil in May 2001. He is a fellow of the Indian Academy of Sciences and a Silver Medalist of the Chemical Research Society of India. His research interests include cycloadditions, radical-mediated C–C and C–heteroatom bond-forming reactions, multicomponent reactions, and heterocyclic synthesis. Forty students have completed Ph.D. degrees under his supervision, and he has published nearly 200 papers in major international journals.

Ani Deepthi was born in Kollam, Kerala State, India, in 1980. She obtained her B.Sc. degree from Kerala University (Fatima Mata National College, Kollam) in 2000 and her M.Sc. degree (First Rank) from the Cochin University of Science and Technology in 2002. She did her doctoral research under the guidance of Dr. Vijay Nair in the Regional Research Laboratory (CSIR) Trivandrum, working in the area of multicomponent reactions and has submitted her Ph.D. thesis to the Cochin University of Science and Technology, Kochi. She is currently working as a postdoctoral fellow in the group of Professor Suresh Valiyaveettil at the National University of Singapore, Singapore.

electron-transfer oxidation involve use of salts of high-valent metals such as Mn(III), Ce(IV), Cu(II), Ag(I), Co(III), V(V), Fe(III), etc. Among these Mn(III) has received considerable attention. In spite of the well-established and frequent use of this reagent for generation of electrophilic carbon-centered radicals from enolic substrates, particularly in intramolecular processes, procedural problems associated with it have prompted development of other oxidants of choice. The availability of Ce(IV) reagents as suitable one-electron oxidants assumes importance at this juncture.

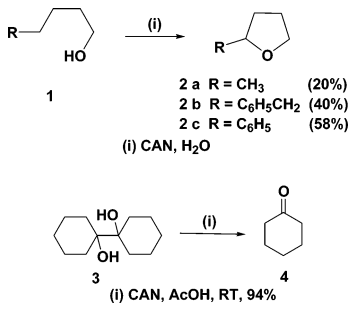
The most extensively used cerium(IV) reagent in organic chemistry is cerium(IV) ammonium nitrate (CAN). The reasons for its general acceptance as a one-electron oxidant may be attributed to its large reduction potential value of +1.61 V vs NHE (normal hydrogen electrode), low toxicity, ease of handling, experimental simplicity, and solubility in a number of organic solvents. CAN has proved to be very useful to synthetic organic chemists for over four decades. The enormous growth in the use of this reagent is evidenced by the publication of a large number of research papers and several reviews concerning CAN-mediated reactions.[25−34] Still, a comprehensive review addressing the synthetic versatility of this reagent has not yet appeared. Hence, we strongly felt the need for a review covering the entire CAN literature. Our earlier reviews in this area have presented brief outlines of CAN-mediated reactions and highlighted the work done in our laboratory.[31,33,34] The present review focuses on the most important synthetic transformations mediated by CAN, covering the literature from 1965 to 2006. Although this review will not detail the material that has already been described in our earlier reviews, some important reactions will be discussed briefly for the sake of completeness.

What makes cerium so unique among the lanthanide elements? The answer lies in the ability of cerium to display stable adjacent oxidation states +3 and +4. The most common oxidation state of the lanthanides is the +3 state. Cerium in its ground state has an electronic configuration of $[Xe]4f^26s^2$, where Xe represents the xenon configuration. The electronic configuration of the Ce^{+3} ion is $[Xe]4f^1$, while that of Ce^{+4} ion is $[Xe]4f^0$. The enhanced stability of the vacant f shell in Ce^{+4} accounts for the ability of cerium to exist in the +4 oxidation state. 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 advent of Ce(IV) reagents in organic synthesis may be attributed to the investigations of Trahanovsky. As early as 1965 he showed that benzyl alcohols underwent oxidation to benzaldehydes in excellent yields using CAN in 50% aqueous acetic acid.[35] The side-chain oxidation of toluene to benzaldehyde by CAN was also reported.[36,37] Trahanovsky also found that oxidation of primary alkanols **1** which possess a δ-H atom produces tetrahydrofuran derivatives **2** (Scheme 1).[38] The fragmentation of 1,2-diols by CAN was also extensively investigated. Mechanistic studies showed that Ce(IV) coordinates with one of the hydroxyl groups followed by one-electron oxidation. Oxidative cleavage of bicyclohexyl-1,1′-diol **3** to cyclohexanone **4** using CAN is illustrative (Scheme 1).[39] More details regarding these investigations are available in an earlier review.[25]

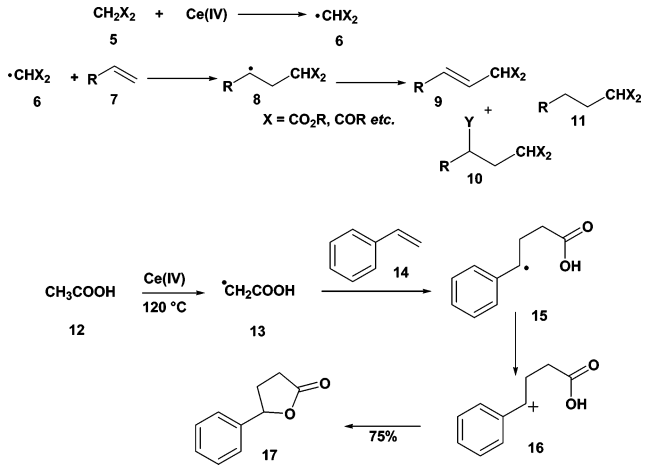
The pioneering work of Heiba and Dessau in 1971 showed that Ce(IV) reagents are useful for C−C bond-forming reactions.[40,41] They illustrated that electrophilic carbon-centered radicals of the type $\bullet CHX_2$ generated by the cerium-

Scheme 1



(IV) oxidation of compounds of the type CH_2X_2, where X is an electron-withdrawing group, viz., CO_2R, COR, etc., can be trapped by various alkenes, resulting in formation of different products. The success of the reaction rests on the selective oxidation of radical **8** by the metal ion. Initially formed radical **6** is not oxidized further due to the electron-withdrawing substituents attached to it. Addition of acetone and aryl ketones to olefins leads to formation of a variety of products. Synthesis of γ-lactones by the Ce(IV)-mediated oxidative addition of carboxylic acids to olefins is illustrated in Scheme 2.[42]

Scheme 2



It may be pointed out that most of the earlier experiments relied on the use of Ce(IV) acetate in acetic acid.[43] Other cerium(IV)-based reagents include cerium(IV) trifluoroacetate,[44a] cerium(IV) methanesulfonate,[44b] and cerium(IV) trifluoromethanesulfonate.[44c] However, procedural problems associated with the use of all these reagents as well as their poor stability led to the use of cerium(IV) ammonium nitrate, which has now emerged as the reagent of choice for various synthetic transformations. Another Ce(IV) reagent which has been developed recently and is finding application in organic synthesis is cerium(IV) tetrabutylammonium nitrate (CTAN). It is prepared by reaction of CAN and tetrabutylammonium hydrogen sulfate in aqueous solution.[45] The advantage of CTAN is that it is soluble in common organic solvents like dichloromethane. Oxidative Prins cyclization of allylsilane-tethered α-stannyl ethers was accomplished using CTAN in 5:2 acetonitrile−dichloromethane.[46] Recently, Flowers and co-workers studied the oxidation reactions of CTAN and observed a solvent-dependent chemoselectivity in the reaction of allyltrimethyl silane with 1,3-dicarbonyl compounds in the presence of CTAN.[47]

Cerium(IV) ammonium nitrate can effect different kinds of transformations. For convenience, this review classifies CAN-mediated reactions into the following categories: (1) reactions involving carbon−carbon bond formation; (2) reactions involving carbon−heteroatom bond formation; (3) reactions involving CAN as a catalytic oxidant; (4) deprotection−protection sequences effected by CAN; (5) miscellaneous transformations. Selected examples from each of the above-mentioned categories are discussed in the following sections.

2. Reactions Involving Carbon−Carbon Bond Formation

Carbon−carbon bond-forming reactions mediated by cerium(IV) ammonium nitrate can be broadly classified into two categories: (i) intermolecular reactions and (ii) intramolecular reactions. Relevant examples of each type are given in the following sections.

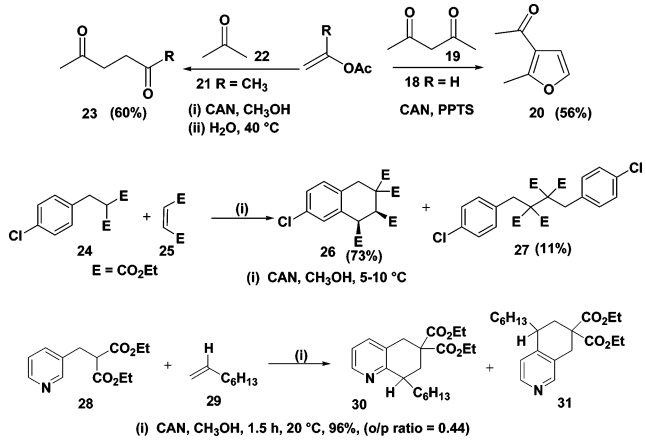
2.1. Intermolecular Carbon−Carbon Bond-Forming Reactions

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. For instance, radicals can be generated from carbonyl and dicarbonyl compounds, silyl enol ethers, styrenes, and other electron-rich systems and can add to different electrophilic bonds. Relevant examples are provided below.

2.1.1. Generation of Carbon-Centered Radicals from Carbonyl and Dicarbonyl Compounds and Related Chemistry

Baciocchi studied the oxidative addition of radicals generated from ketones and 1,3-dicarbonyl compounds by CAN to olefins such as isopropenyl acetate **21** or vinyl acetate **18** and observed formation of 1,4-diketones[48] or furan derivatives,[49] respectively. Oxidation of substituted diethyl α-benzyl malonate **24** by CAN in the presence of substituted olefins resulting in formation of highly functionalized tetrahydronaphthalenes was studied by Citterio and co-workers. Subsequently, these authors utilized the same strategy in the synthesis of substituted tetra- or dihydroisoquinolines by the CAN-mediated reaction of diethyl(pyridylmethyl) malonate **28** in the presence of alkenes and alkynes (Scheme 3).[50,51]

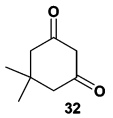
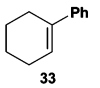
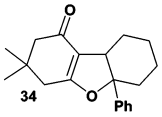
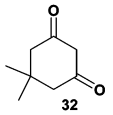
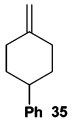
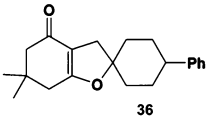
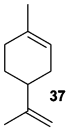
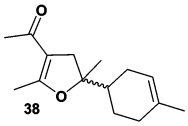
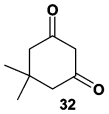
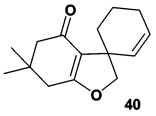
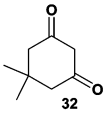
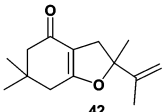
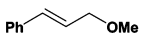
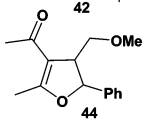
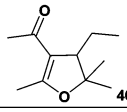
Scheme 3



Extensive investigations on CAN-mediated addition of active methylene compounds to olefins carried out by Nair

and co-workers have uncovered many interesting reactions. It has been shown that reaction of 1,3-dicarbonyl compounds with unactivated alkenes in the presence of CAN constitutes a facile route to dihydrofuran derivatives.[52] This protocol was found to be general with a variety of dicarbonyl compounds and alkenes (Table 1). With exocyclic alkenes

Table 1. CAN-Mediated Oxidative Addition of 1,3-Dicarbonyl Compounds to Alkenes[a]

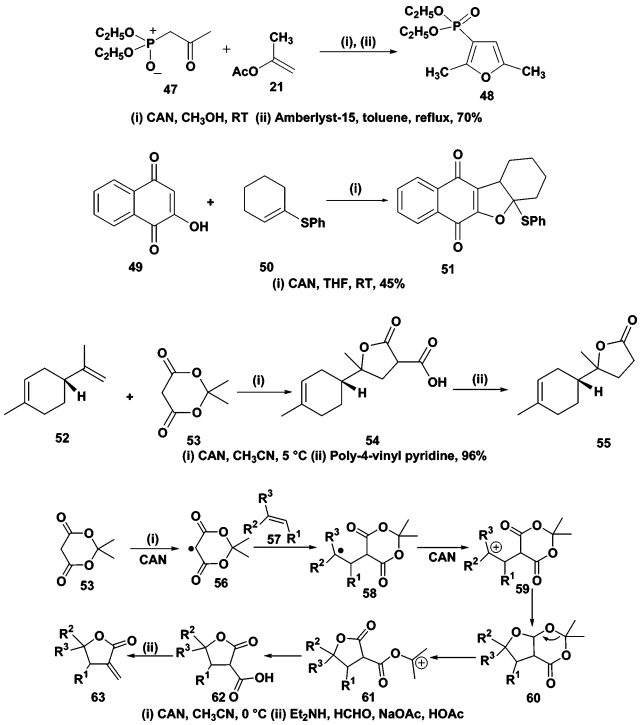
Entry	Dicarbonyl compound	Alkene	Product	Yield (%)
1	 32	 33	 34	98%
2	 32	 Ph 35	 36	77%
3	 19	 37	 38	46%
4	 32	 39	 40	55%
5	 32	 41	 42	70%
6	 19	 43	 44	85%
7	 19	 45	 46	60%

[a] Reaction conditions: CAN (2 equiv), MeOH, 5 °C, 15 min.

such as **35**, the corresponding spirodihydrofurans were isolated.[53] CAN-mediated addition of active methylene compounds to dienes in methanol also led to the synthesis of dihydrofuran derivatives. The reaction was found to be general with cyclic as well as acyclic dienes.[54,55] Table 1 highlights the results of the investigations in this area. The reaction requires two equivalents of CAN for completion. Mechanistically, the reaction involves the CAN-mediated generation of the radical from the 1,3-dicarbonyl compound which gets trapped by the olefin to generate an intermediate radical, which subsequently gets oxidized to the cation by the second equivalent of CAN and finally cyclizes to yield the dihydrofuran. Subsequently, Roy and co-workers have shown that 1,3-dicarbonyl compounds undergo facile addition to cinnamic esters as well as cyclic enol ethers to afford the corresponding dihydrofurans.[56]

Hong and co-workers applied this strategy for the synthesis of several nitrated dicyclopentadiene and norbornadiene derivatives by oxidative addition of malonyl radical to dicyclopentadiene followed by a Wagner−Meerwein rearrangement.[57] Further extension of the protocol for the synthesis of substituted diethyl-3-furyl phosphonates by the CAN-induced oxidative addition of β-ketophosphonate **47** to vinyl acetate **21** followed by acid-catalyzed cyclization is also reported.[58] Dihydrofuran substituted with sulfide group **51** was synthesized by the CAN-mediated oxidative addition of 1,3-dicarbonyl compound to vinyl sulfide.[59] A short two-step synthesis of norbisabolide **55**, a C-12 terpene lactone, was achieved by oxidative addition of Meldrum's acid to (*R*)-(+)-limonene using CAN followed by decarboxylation with poly-4-vinylpyridine (Scheme 4).[60] A facile two-step

Scheme 4

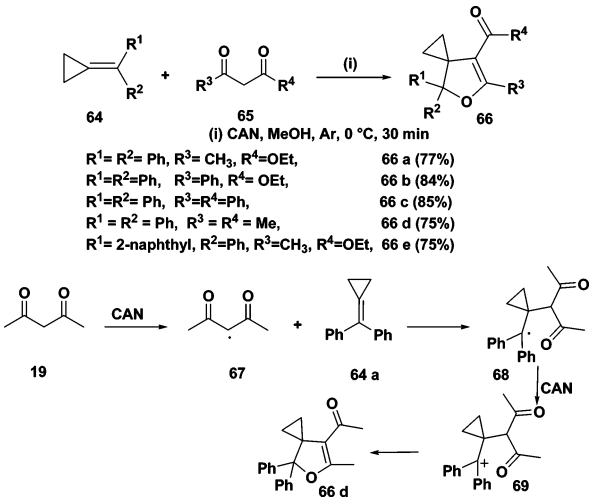


procedure for the synthesis of α-methylene lactone **63** by reaction of alkenes and Meldrum's acid mediated by CAN was developed very recently. The reaction occurs by initial addition of the radical generated from Meldrum's acid by CAN to the alkene followed by a decarboxylative methylenation to afford the product **63**. Mechanistic rationale for this reaction is shown in Scheme 4.[61]

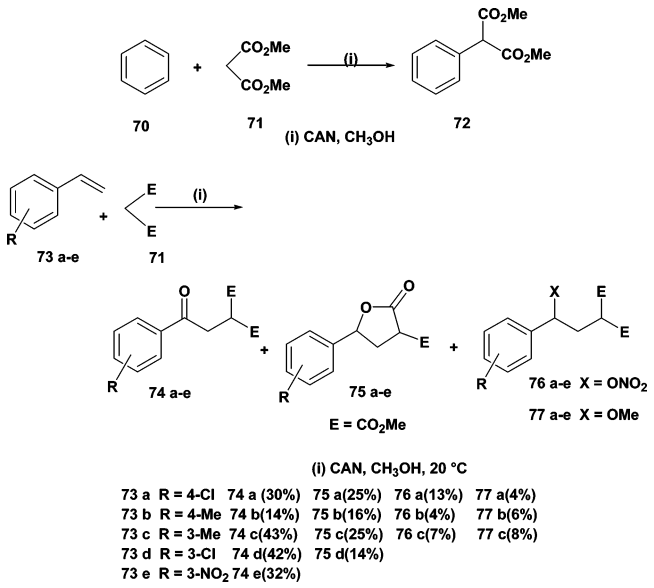
Oxidative addition of 1,3-dicarbonyl compounds to methylenecyclopropanes (MCPs) **64** using CAN afforded spirocyclopropyl dihydrofuran derivatives in good yields. Cyclic 1,3-dicarbonyl compounds also gave analogous results. The mechanism of this reaction involves the CAN-mediated generation of a radical from acetyl acetone **19**, which is trapped by MCP **64**, giving the intermediate radical **68**. In the second step the radical **68** is oxidized to cation **69** by the second equivalent of CAN. The latter then undergoes cyclization to afford the dihydrofuran **66** (Scheme 5).[62]

Electrophilic addition of carbon-centered radicals produced by the CAN-mediated oxidation of dimethyl malonate to olefinic double bonds and aromatic systems has been well studied. CAN-mediated malonylation of aromatic compounds in methanol is a typical example (Scheme 6). Similarly, thiophenes, furans, and their benzo analogs undergo facile malonylation in the 2 position on treatment with excess dialkylmalonate and ceric sulfate in methanol.[63,64] A mechanistically fascinating reaction was observed in the addition of dimethyl malonate **71** to styrene **73**. Formation of product **74** is probably initiated by the trapping of oxygen by the

Scheme 5

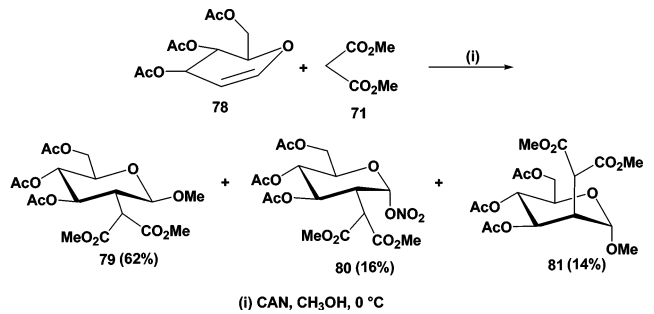


Scheme 6



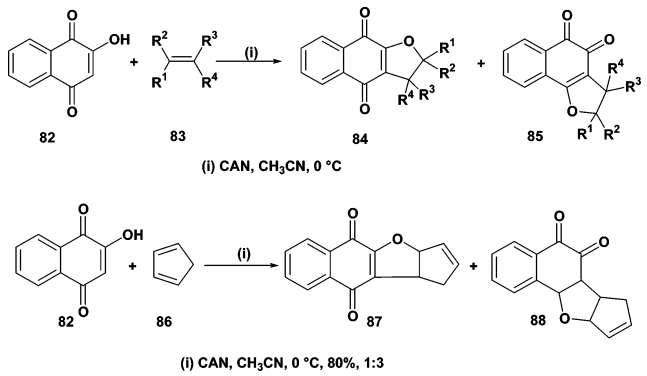
intermediate benzylic radical. Transformation of the benzylic radical to the hydroperoxide followed by lactonization of the resultant carbinol can account for the product **75**. Formation of **76**/**77** may be rationalized by addition of nitrate or methoxide anion to the benzylic cation (Scheme 6).[65] The ability of CAN to form radicals from malonates under very mild conditions was effectively utilized by Linker for the synthesis of C-2-branched sugars by the CAN-induced addition of malonate to glycals (Scheme 7).[66]

Scheme 7



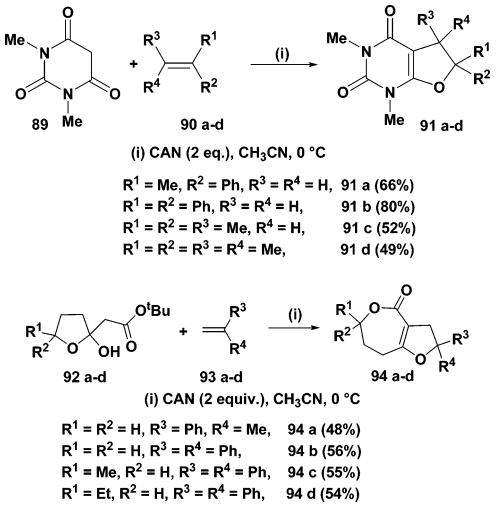
CAN-mediated addition of dimethyl malonate to 2-benzyl-1,4-napthoquinone resulted in formation of naphthacene-5,-12-diones.[67] The radical generated from 2-hydroxy-1,4-naphthoquinone **82** by CAN has been utilized in the [3+2] cycloaddition of this species to alkenes resulting in formation of furo-*p*-quinones as well as *o*-quinone derivatives. The radical formed by the initial addition to the alkene gets oxidized to a cation by the second equivalent of CAN and subsequently gets quenched intramolecularly by the hydroxyl group to afford the product. Similar oxidative addition of **82** to dienes offered a simple and rapid one-step procedure for the synthesis of naphthofurandiones (Scheme 8).[68,69] The

Scheme 8



[3+2] cycloaddition strategy was further elaborated by Kobayashi and co-workers for the synthesis of phenalenofuranones,[70] furopyranones, and furoquinolinones.[71] Dihydrofuropyrimidinediones **91** were formed with complete regioselectivity by the [3+2] cycloaddition of pyrimidine trione with alkenes (Scheme 9).[72] Very recently, synthesis

Scheme 9

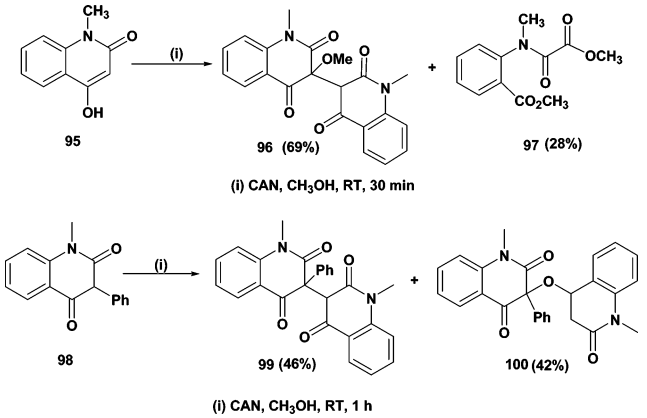


of tetrahydrofuro[3,2-*c*]oxepin-4(6*H*)-ones **94** was achieved by reaction of 2-(2-hydroxytetrahydrofuran-2-yl)acetates with alkenes (Scheme 9).[73]

All reactions discussed so far are based on trapping the electrophilic carbon-centered radicals generated by CAN using electron-rich substrates. In addition, these radicals are also susceptible to dimerizations. 1,3-Dicarbonyl compounds were dimerized chemically by CAN or electrocatalysis using nitrate as a mediator. Oxidative homocoupling of diethyl malonate to tetramethyl ethane-1,1,2,2-tetracarboxylate was achieved in the presence of CAN and magnesium oxide.[74] CAN-mediated dimerizations of 4-hydroxyquinolin-2-(1*H*)-one **95** and 3-phenyl 4-hydroxyquinolin-2-(1*H*)-one **98**

have been studied. Reaction of **95** with two equivalents of CAN in methanol at room temperature afforded the quinolin-2(1*H*)-one dimer **96** together with smaller amounts of oxalamate **97**. An unexpected product **100** was formed in the second case showing the ambident reactivity of the α,α′-dicarbonylalkyl radicals as carbon- and oxygen-centered radical (Scheme 10).[75] Nicolaou applied this strategy for the

Scheme 10



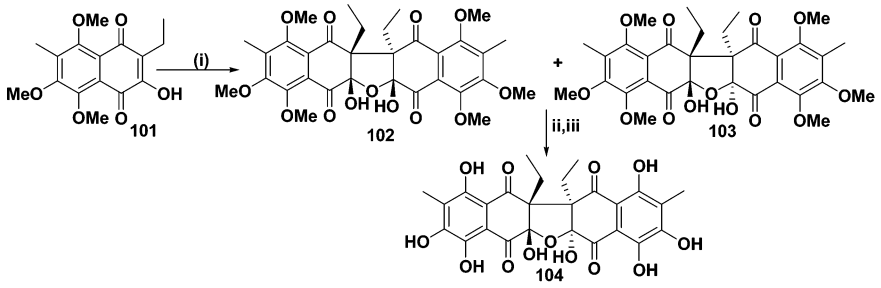
synthesis of the racemic hybocarpone based on CAN-promoted oxidative dimerization of naphthazirin (Scheme 11).[76]

2.1.2. Generation of Carbon-Centered Radicals from Silyl Enol Ethers and Related Chemistry

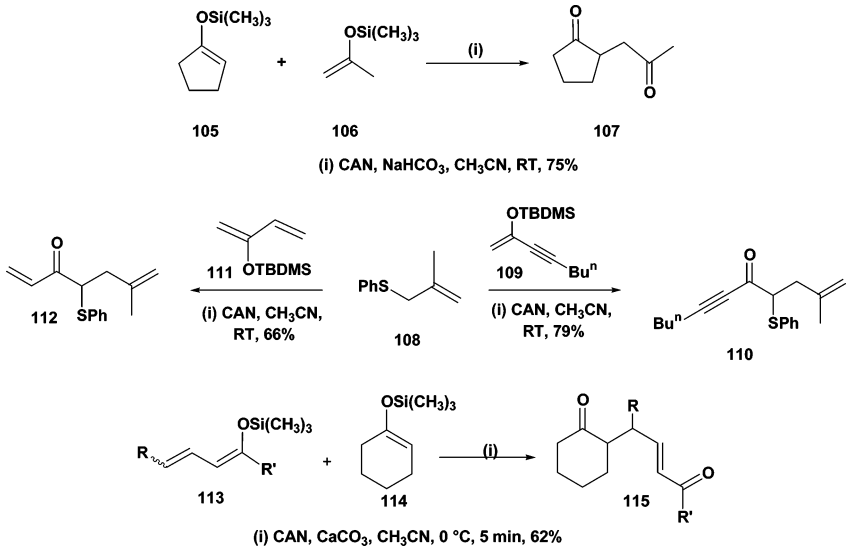
Silyl enol ethers constitute another class of substrates which are ideal for CAN-mediated oxidative generation of carbon-centered radicals. This protocol serves as an efficient method for generation of α-ketoalkyl radicals by CAN. Baciocchi has shown that CAN-mediated oxidative coupling of 1,2- and 1-substituted silyl enol ethers leads to an efficient synthesis of 1,4-diketones.[77] The success of the reaction rests on the relative ease of oxidation of the 1,2-disubstituted silyl enol ether vis a vis the monosubstituted one. For instance, **105** is more easily oxidized than **106** (Scheme 12). The cation radical generated from allyl phenyl sulfides such as **108** reacts with silyl enol ether, siloxy diene, and siloxy enyne to give α-phenylthio-γ,δ-unsaturated ketones. The reaction occurs presumably via nucleophilic addition of silyl enol ether to the sulfur cation radical followed by [2,3] sigmatropic rearrangement (Scheme 12).[78] Similarly, CAN-mediated oxidative addition of enamines to electron-rich olefins such as silyl enol ethers constitutes a facile synthesis of 1,4-dicarbonyl compounds.[79] It has been reported that oxidative addition of silyl dienol ethers to silyl enol ethers promoted by CAN comprises a convenient method for the synthesis of 6-oxo-α,β-unsaturated carbonyl compounds **115**.[80]

In addition to activated alkenes, simple conjugated dienes have also been employed as efficient traps for carbon radicals generated by Ce(IV) oxidation of silyl enol ethers. A generalized reaction is shown in Scheme 13. Tandem additions of such radicals to dienes followed by Pd(0)-catalyzed alkylation of the resulting nitroxy adducts serve as a valuable synthetic route to highly functionalized (*E*)-γ,δ-unsaturated carbonyl compounds.[81] It has been reported that α-nitroalkyl radical generated by oxidation of nitronate anion with CAN adds to electron-rich olefins like silyl enol

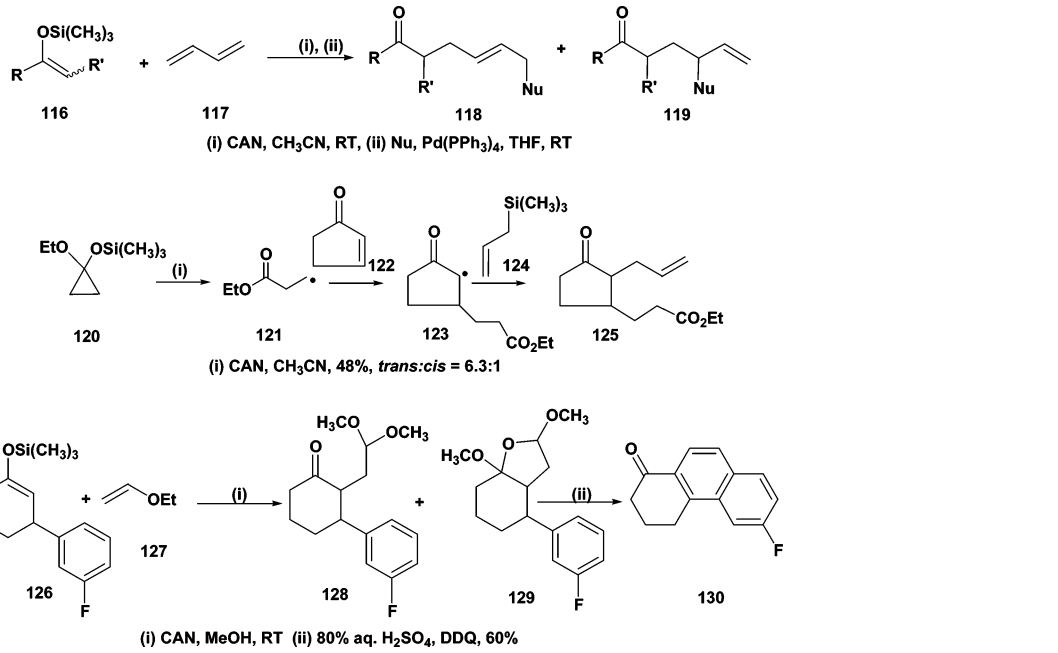
Scheme 11



Scheme 12



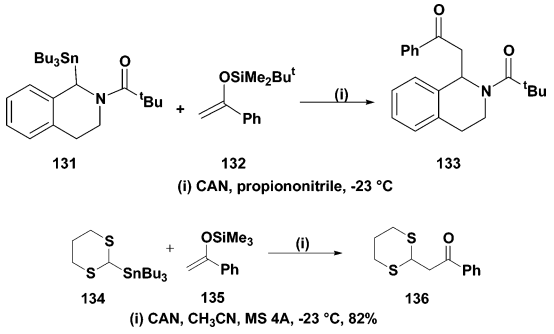
Scheme 13



ethers to afford β-nitroketones.[82] β-Carbonyl alkyl radicals generated by the CAN-induced fragmentation of 1-ethoxy-1-trimethylsilyloxy cyclopropane **120** add to α,β-unsaturated cycloalkenones in the presence of electron-rich olefins, thus providing ready access to 2,3-disubstituted cycloalkanones (Scheme 13).[83] On the basis of this strategy, a simple approach to 3,4-dihydro-(2*H*)phenanthrene-1-one **130** was effected by the oxidative addition of 3-aryl-1-(trimethysilyl)-oxycyclohexenes to ethyl vinyl ether.[84]

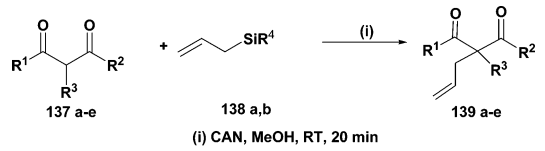
Oxidative addition of stannyl compounds mediated by CAN to silyl enol ethers has also been reported. Addition of radicals generated by the CAN oxidation of *N*-1-tributylstannyl alkyl carboxamide **131** and 2-tributylstannyl 1,3-dithiane **134** to silyl enol ether, reported by Narasaka and co-workers, yielding products such as **133** and **136**, is illustrated in Scheme 14.[85]

Scheme 14



Reaction of 1,3-diketones, β-keto esters, and malonates with allyltrimethylsilane in the presence of CAN in methanol was studied by Hwu and co-workers. The reaction afforded the mono-C-allylated products in good yields (Scheme 15). It is noteworthy that when $Mn(OAc)_3$ was used as the oxidizing agent in these reactions, silicon-containing dihydrofurans were formed as products, probably because the reactivity of $Mn(OAc)_3$ is not high enough to oxidize the intermediate β-silyl radical, and therefore, it underwent cyclization. Heiba and Dessau reported a reactivity ratio of

Scheme 15



R^1= Me, R^2= OEt, R^3= H, R^4=Me,	139 a (84%)
R^1= R^2= t-Bu, R^3= H, R^4= Me,	139 b (98%)
R^1= R^2= Ph, R^3= Me, R^4= Me,	139 c (91%)
R^1= Me, R^2= OEt, R^3= H, R^4= Me_2Ph	139 d (80%)
R^1= R^2= OEt, R^3= H, R^4= Me	139 e (74%)

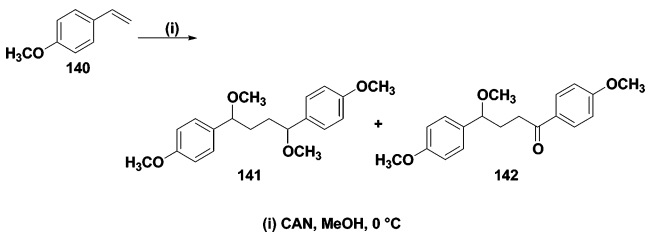
12:1 for the Ce(IV)- and Mn(III)-mediated oxidations of secondary alkyl radicals.[32,86]

2.1.3. Generation of Radical Cations from Styrenes and Related Chemistry

Baciocchi et al. reported formation of dinitrates from styrene under photochemical or thermal conditions using CAN in acetonitrile. Dinitrates are formed by addition of nitrato radicals across the double bond.[87]

More recently, Nair and co-workers have shown that styrenes displayed multiple reactivity toward CAN depending on the nature of substituents on the benzene ring. For instance, 4-methoxy styrene **140** underwent facile dimerization to yield **141** and **142** with CAN in methanol (Scheme 16).[88] Table 2 summarizes the results obtained under different

Scheme 16



reaction conditions. On the other hand, styrenes devoid of any alkoxy groups on the benzene ring reacted in the presence of CAN in methanol to afford α-methoxy acetophe-

Table 2. Reaction of 4-Methoxy Styrene with CAN in Methanol

entry	reaction conditions	141	142
1	CAN/MeOH, air, 0 °C	10%	53%
2	CAN/MeOH, oxygen, 0 °C	16%	62%
3	CAN/MeOH, argon, 0 °C	60%	8%

nones.[89] It is noteworthy that alternative methods for generation of α-methoxy acetophenones include BF_3·OEt_2-catalyzed reaction of diazoketones and alcohols, oxidation of alkenes with peracetic acid, OsO_4/Ni(II) complex, and permanganate/$CuSO_4$ reagent combination. Evidently, the CAN-mediated reaction is much milder and simpler when compared to these methods. Interestingly, 3,4-dimethoxy styrene, when subjected to identical reaction conditions, afforded the tetralone derivative **146** and naphthalene derivative **147** in addition to the linear products **144** and **145**. Table 3 summarizes the results under different reaction conditions.

Table 3. Reaction of 3,4-Dimethoxy Styrene with CAN in Methanol

entry	reaction conditions	144	145	146	147
1	CAN/MeOH, air, 0 °C	15%	12%	59%	8%
2	CAN/MeOH, oxygen, 0 °C			65%	10%
3	CAN/MeOH, argon, 0 °C	36%			37%

A mechanistic rationale can be invoked along the following lines (Scheme 17). The initial event involves oxidative electron transfer from styrene to Ce(IV) to afford the radical cation **I**. This would, in turn, add to another molecule of styrene to generate a distonic radical cation **II**. The cationic center of **II** will be quenched by nucleophilic solvents like methanol, whereas the radical center can react with oxygen from the atmosphere, affording the ketomethoxy product **145**. Alternatively, further oxidation of this radical by Ce(IV) to a cation followed by addition of nucleophilic solvents can afford the dimethoxy product **144**. The 1,4-cation radical **II** can also undergo 1,6-cyclization to give a substituted hexatriene radical cation **IV**, which can eventually lose a proton to yield a radical intermediate **V** that gets converted to the tetralone **146**. Alternatively, the hexatriene radical cation undergoes aromatization to afford the naphthalene derivative **147**. In the case of styrenes devoid of alkoxy groups, presumably the reaction involves addition of oxygen diradical to the benzylic radical cation generated by CAN oxidation of styrene followed by quenching with methanol to yield α-methoxy acetophenone.[89]

Subsequent study of the reactivity of styrenes with CAN carried out in acetonitrile as solvent was found to yield tetralin derivatives. For instance, reaction of 4-methylstyrene with CAN in acetonitrile afforded the α-acetamidotetralins *cis*-**149** and *trans*-**149** in good yields. The acetamidotetralins were formed by oxidation of the radical intermediate analogous to **VIII** to the cation, which is trapped by the solvent acetonitrile in a Ritter fashion. It is noteworthy that 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. Special mention may be made of the top-selling antidepressant Sertraline (Figure 1). The reaction was found to be general with a

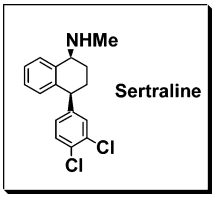


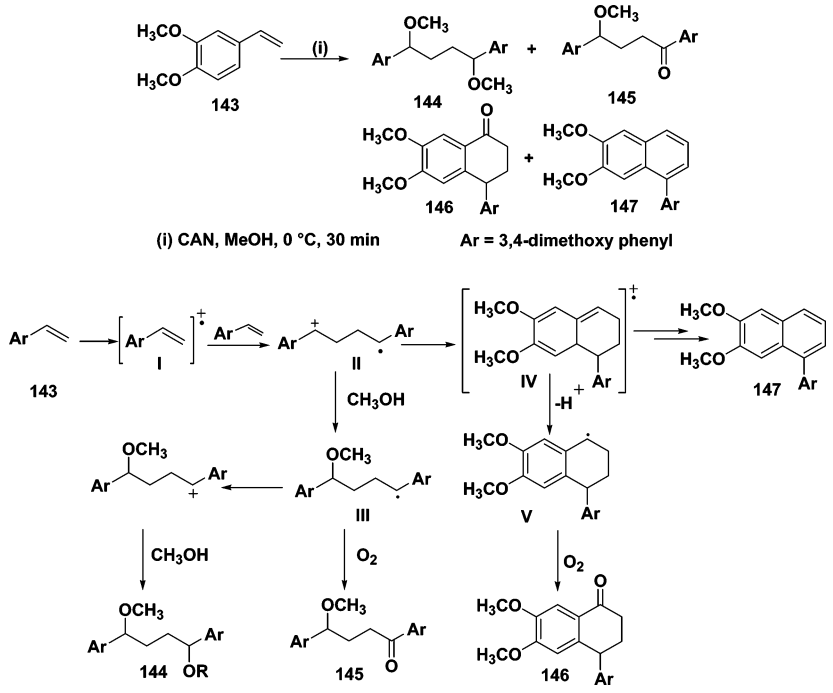
Figure 1.

variety of styrenes and vinyl naphthalenes. α-Acrylamidotetralins were obtained when acrylonitrile was used as the solvent (Scheme 18).[90]

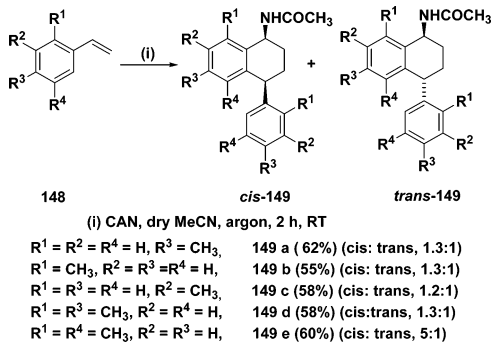
2.1.4. Generation of Cation Radicals from Electron-Rich Aromatic Systems and Related Chemistry

CAN-mediated nitromethylation, acetonylation, and malonylation of aromatic systems have been reported in the literature.[91,92] The CAN-mediated oxidation of 5-hydroxy-

Scheme 17

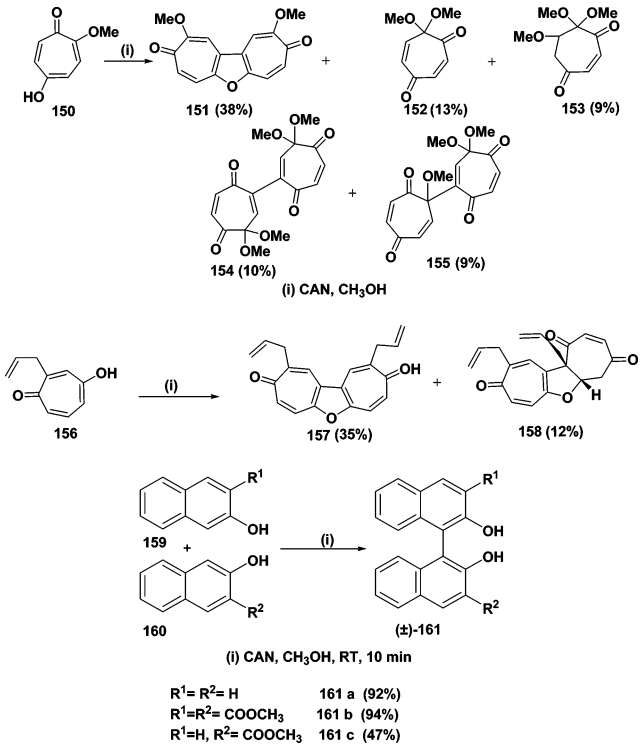


Scheme 18



2-methoxytropone **150**[93] and 4-hydroxy tropone **156**[94] afforded the corresponding dimeric products. Oxidative coupling of naphthols **159** and **160** in the presence of cerium(IV) ammonium nitrate afforded (±)-binaphthols **161**[95] in excellent yields (Scheme 19). Oxidative dimerization of

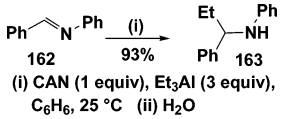
Scheme 19



naphthazirin is depicted in Scheme 11.[76]

Very recently, ethylation of a variety of imines at the methine moiety was accomplished at room temperature by CAN-promoted coupling of imines with triethyl aluminum (Scheme 20). However in the absence of excess triethyl

Scheme 20

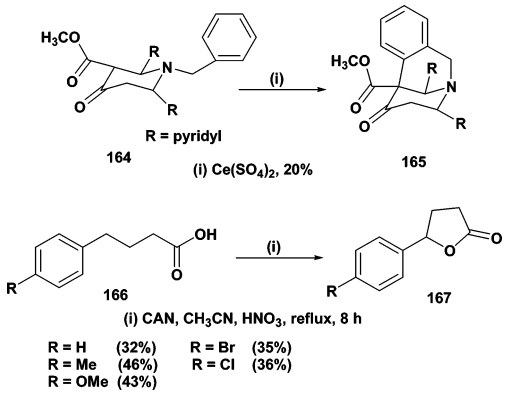


aluminum, CAN promoted the hydrolysis of the unreacted Schiff base to the corresponding aldehyde presumably by a redox process involving the nitrate groups of CAN and the disproportionated ethylation reagent.[96]

2.2. Intramolecular Carbon–Carbon Bond-Forming Reactions

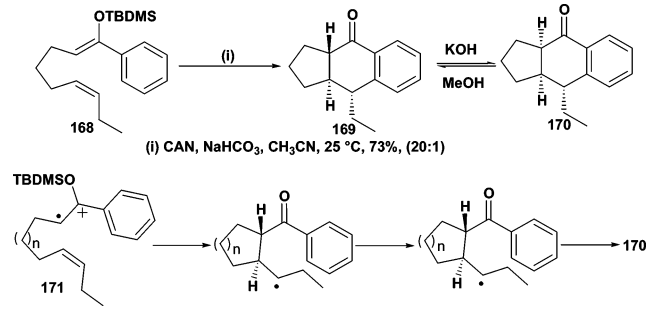
In contrast to the prevalent use of CAN in several intermolecular reactions, its potential in facilitating intramolecular reactions has remained largely unexplored for many years. However, very recently a number of intramolecular reactions based on CAN oxidation have been reported. The first report on Ce(IV)-promoted intramolecular reaction involves the cyclization of 1-benzyl-2,6-bis-[2′-pyridyl]-4-piperidone-3-carboxylic acid methyl ester **164** mediated by Ce(IV) sulfate albeit in very low yields.[97] Oxidation of γ-phenyl butanoic acids **166** with CAN in acetonitrile resulted in formation of the corresponding butyrolactones as the only isolable products in moderate yields. Formation of butyrolactones is not surprising as Heiba and Dessau had shown in 1971 that carboxyl radicals add to styrenes and the resulting radical cyclizes to form γ-lactones (Scheme 21).[98]

Scheme 21



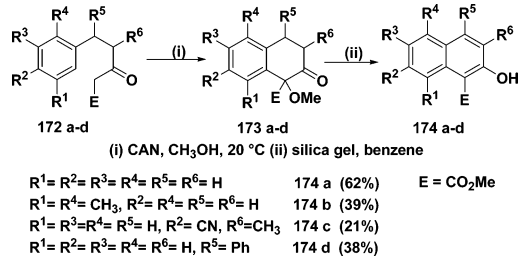
Snider reported isolated examples of oxidative cyclization of δ, ϵ and ϵ, ϕ unsaturated silyl enol ethers by CAN affording tricyclic ketones in high yields and excellent diastereocontrol. Mechanistically the tandem cyclization occurs by two one-electron oxidations, two cyclizations, and loss of silyl group. Presumably the reaction occurs via formation of a highly electrophilic cation radical **171** which cyclizes to give **170**. Final cyclization to form the tetralone ring occurs at either the cation or radical oxidation states (Scheme 22).[99]

Scheme 22



2-Hydroxy-1-naphthoic acid esters **174** and amides were synthesized by the CAN-promoted cyclization of 5-aryl-3-oxo-pentanoic acid esters **172** or amides (Scheme 23).[100] On the other hand, CAN-induced oxidative cyclization of dimethyl-4-pentenyl malonate in methanol as well as acetic acid occurred with poor selectivity, leading to several products.[101]

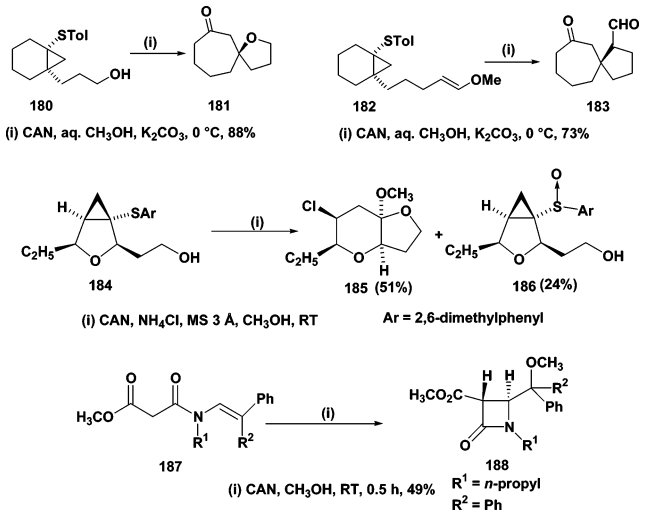
Scheme 23



Single-electron transfer (SET) oxidation of cyclopropylsulfides by CAN leading to the synthesis of cyclic ethers and spirocyclic compounds has been extensively studied by Takemoto and co-workers. Cyclopropyl sulfides having a hydroxyl group in the side chain underwent CAN-mediated tandem ring cleavage and subsequent cyclization giving cyclic ethers. SET oxidation of **175** initially generates the cation radical intermediate **A**, which can undergo further transformations via two pathways. In route a, nucleophilic attack on the more hindered β-carbon by the hydroxyl group followed by another SET oxidation and quenching of the sulfonium ion **B** by methanol leads to **D**. The other pathway involves the initial ring opening (route b) via **C**. This is followed successively by nucleophilic addition of the solvent, SET oxidation, and then cyclization of **C** to the desired cyclic ether **D**. Finally, in both cases, **D** is solvolyzed by methanol or water to produce the ketone **177** (Scheme 24).[102]

Asymmetric synthesis of oxaspiro undecanone has been achieved by the oxidative ring expansion and cyclization of optically active bicyclo[4.1.0]heptyl sulfides having a hydroxy substituent in the side chain such as **180** (Scheme 25).[103] Similarly, a facile stereoselective synthesis of *cis*-fused chlorinated bicyclic ethers has been achieved byoxidative ring opening of cyclopropylsulfides of the type **184** (Scheme 25).[104] In an extension of this work, it was shown that cyclopropyl sulfides possessing two pendent side chains endowed with hydroxyl groups can form tricyclic ethers; the

Scheme 25



results are shown in Table 4.[105] However, intramolecular [3+2] cycloaddition of cyclopropyl sulfides with alkenes mediated by CAN seems to be of negligible synthetic value due to the low yield and poor stereoselectivity.[106] Similar to the oxidative ring expansions of cyclopropyl sulfides, ring expansion reactions of cyclopropyl amines have also been reported. For instance, 5-exo cyclization of tertiary amino cyclopropanes with suitably tethered olefins led to formation of bicyclic products.[107] CAN-mediated 4-exo-trig cyclization of α-carbonyl radicals generated from substituted enamides such as **187** offered an expeditious route to functionalized β-lactams as shown in the Scheme 25.[108] Very recently, the ability of CAN to open up the cyclopropyl moiety was utilized for the synthesis of benzotropolones by Hasegawa and co-workers.[109]

Cyclization of δ-aryl-β-dicarbonyl compounds to β-tetralones was accomplished by Rickards using both manganese(III) acetate and CAN. Methoxylated tetralone **198** was obtained via the secondary oxidation at the benzylic position of the initially formed enolizable tetralone (Scheme 26).[110]

Scheme 24

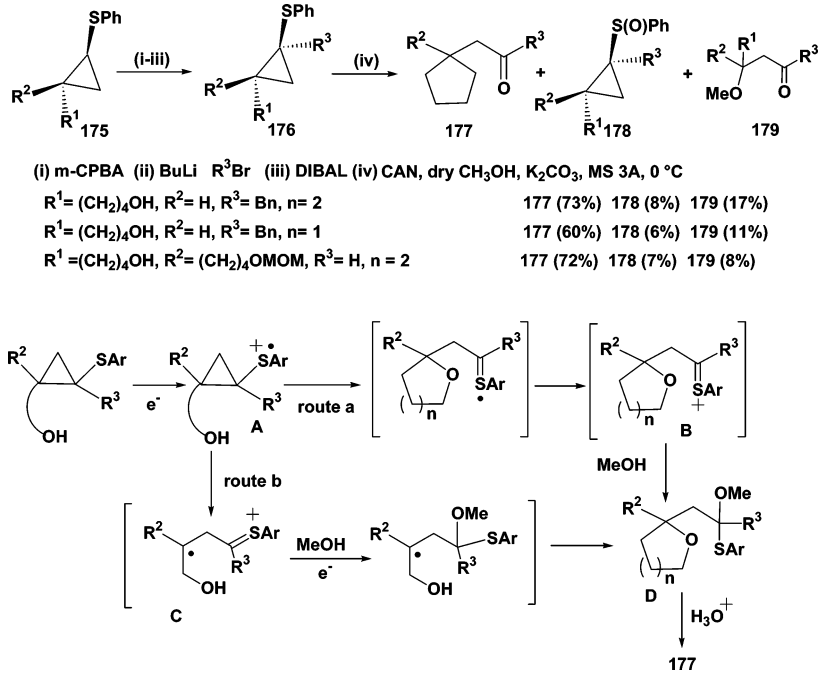
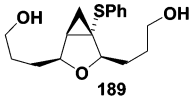
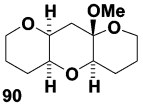
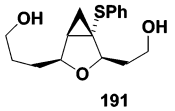
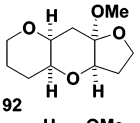
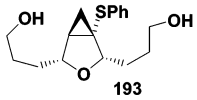
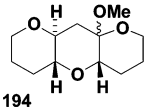
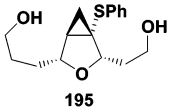
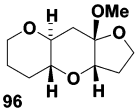
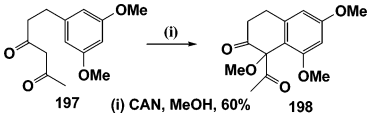


Table 4. Synthesis of Tricyclic Ethers from Cyclopropyl Sulfides by CAN Oxidation[a]

Entry	Substrate	Product	Yield (%)
1	 189	 190	70%
2	 191	 192	62%
3	 193	 194	80%
4	 195	 196	68%

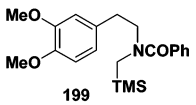
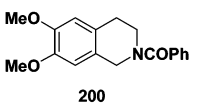
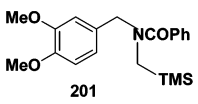
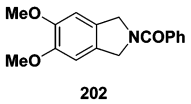
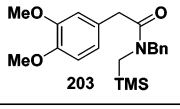
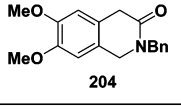
[a] Reaction conditions: CAN, MeOH, Me_4HCl, 3 Å MS, rt, 70%.

Scheme 26



Another interesting intramolecular cyclization reaction mediated by CAN is conversion of phenethylamide **199** to the dihydroisoquinoline **200**. In this reaction, CAN promotes an oxidative Pictet Spengler cyclization of silicon-substituted amine and amide substrates via generation of *N*-alkyl and *N*-acyliminium cations. Chain-shortened aryl methyl amide **201** exhibited lower efficiency due to the competitive iminium cation hydrolysis (Table 5).[111]

Table 5. Intramolecular CAN-Mediated Cyclization of Phenethylamides[a]

Entry	Substrate	Product	Yield (%)
1	 199	 200	60%
2	 201	 202	7%
3	 203	 204	50%

[a] Reaction conditions: CAN, dry CH_3CN, 8 h.

The radical generated by oxidation of the aci-nitro anion formed from **205** underwent intramolecular cyclization, leading to stereoselective formation of 3,4-functionalized tetrahydrofuran derivatives **206** and **207** (Scheme 27). The high stereoselectivities observed in this reaction are indicative of the 5-exo-trig-radical cyclization rather than an intramolecular [3+2] cycloaddition, which can also be invoked here. This protocol was also used for the preparation of tetrahydropyrans by suitably adjusting the length of the alkenyl tether.[112,113] On treatment with CAN in acetonitrile intramolecular cyclization of unsaturated ketene dithioacetal **208** to the corresponding bicyclic lactone **209** occurred. Ketene dithioacetal **210**, however, did not react, indicating that a moderately electron-rich double bond was needed for oxidative cyclization to occur (Scheme 27).[114]

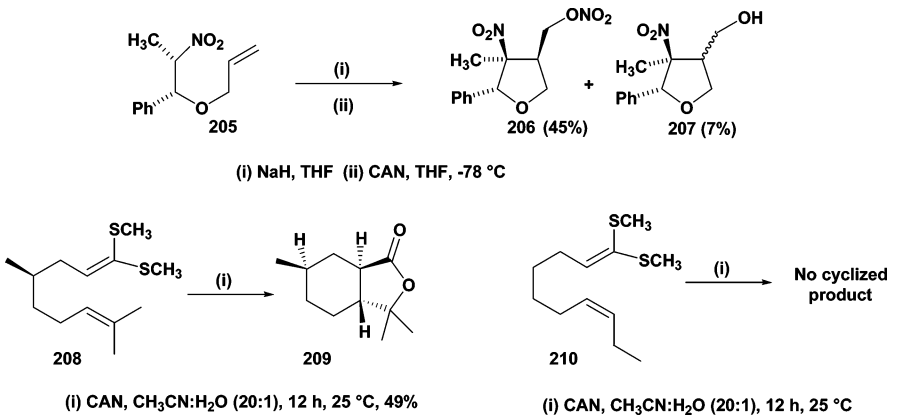
Recently, a novel oxidative cyclization of 1,3-bis(trimethylsilyloxy)buta-1,3-dienes mediated by CAN leading to regioselective formation of functionalized 1,4-dihydroquinones was reported. The 'head−head' regioselectivity exhibited by the CAN oxidation of **211** may be rationalized by considering that attack at the γ position of radical **B** leads to the most stabilized carbonyl conjugated α-silyloxy radical **C**. Oxidation and extrusion of the second silyl group results in formation of intermediate **E**. Cyclization, oxidation, and extrusion of the fourth silyl group affords intermediate **F**, which is subsequently oxidized to the final product **213** (Scheme 28).[115]

An intramolecular version of the reaction of alkoxy styrenes with CAN was accomplished using suitably substituted dicinnamyl ethers. The reaction of trimethoxy cinnamyl cinnamyl ether **214** with CAN in methanol resulted in stereoselective formation of the corresponding 3,4-*trans*-disubstituted tetrahydrofuran derivative **215** in moderate yield. A marginal increase in the yield was noticed when the reaction was carried out under oxygen atmosphere. Under argon atmosphere, the reaction afforded the corresponding tetrahydrofuran derivatives as a mixture of methoxy and nitrato derivatives **216** and **217** in a ratio of 2:1 in high yields.[116] Mechanistically, the reaction may be considered to involve oxidation of the methoxy styrene moiety of ether **214** to afford a radical cation **I**, which can presumably exist in equilibrium with its distonic cyclic version **III**. Arguably, formation of the stable benzylic radical is the major driving force for this 5-exo-cyclization process. The cationic center of **III** gets quenched by the solvent, whereas the radical center is prone to two different transformations. Under oxygen atmosphere, **III** is intercepted by molecular oxygen, affording the keto-product **215**. Under argon atmosphere, **III** gets oxidized by another equivalent of CAN to the benzylic cation with subsequent addition of methanol to afford the dimethoxy product **217**. Alternatively, ligand transfer from CAN would lead to the nitrato derivative **216** (Scheme 29).

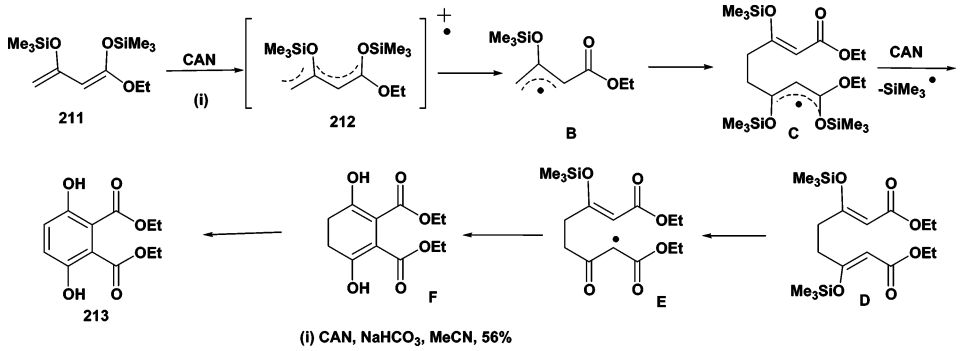
Subsequent work by Floreancig has shown that homobenzylic ethers with pendent enolacetate moiety can undergo highly efficient cleavage followed by 6-endo cyclization in the presence of CAN to afford tetrahydropyrones with excellent stereocontrol.[117] The effect of olefin substitution on the cyclization efficiency is depicted in Table 6. It was found that olefin geometry is retained during the cyclization (entry 1) and that trisubstituted olefins are also effective substrates for the process (entry 2). Allyl silyl ethers are tolerated in the reaction despite the possibility for a competition via vinylogous pinacol rearrangement following oxocarbenium ion formation. However, a simple vinyl group (entry 4) did not sufficiently weaken the benzylic C−C bond to promote cleavage and cyclization with the alternative reaction pathway of nucleophilic attack by nitrate on the aromatic nucleus to form product **225** being the only discerned process.[118]

Enamide esters such as **226** were reported to undergo 5-endo cyclization in the presence of CAN to yield disubstituted γ-lactams in moderate yields. The reaction occurs by oxidative addition of the radical generated from the active methylene of **226** to the olefin culminating in a 5-endo

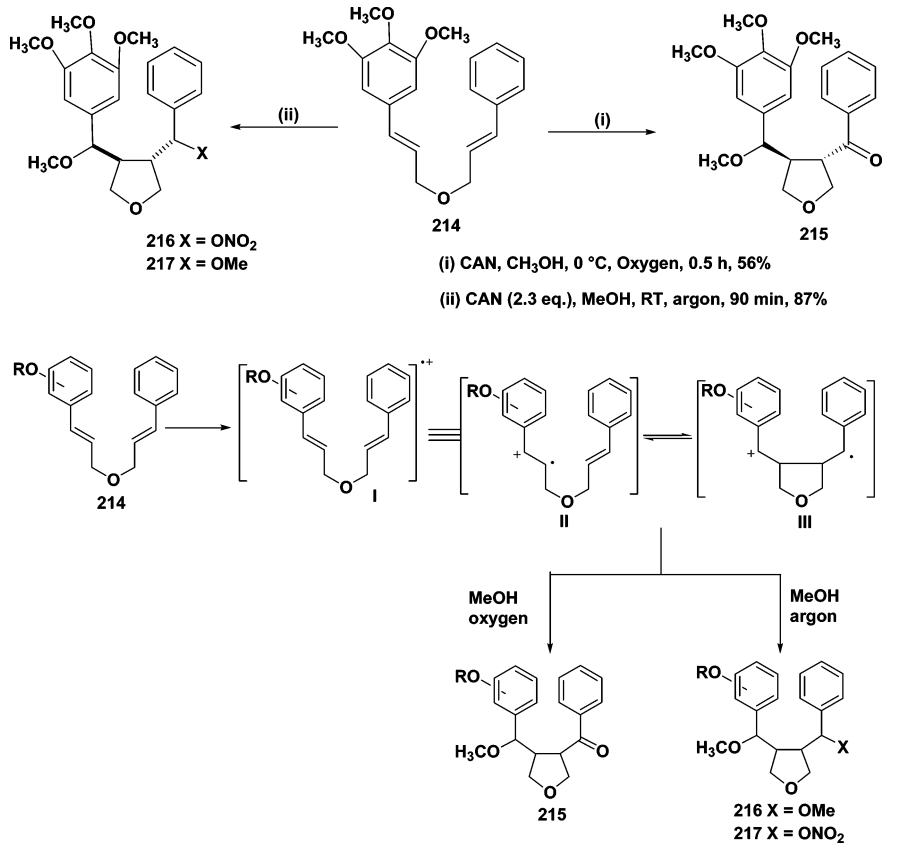
Scheme 27



Scheme 28



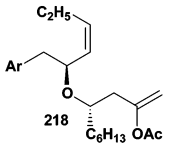
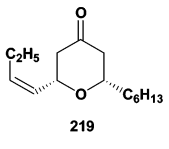
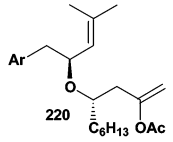
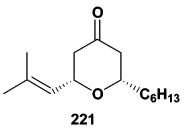
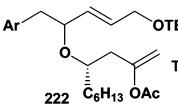
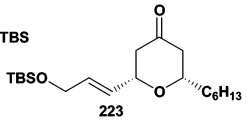
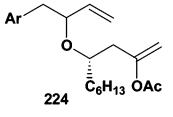
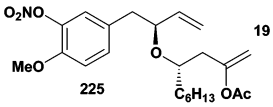
Scheme 29



cyclization. This method has been used to synthesize the basic heterocyclic ring fragments of the natural products L-755,807, Quinolacticin C, and PI-091 (Scheme 30).[119]

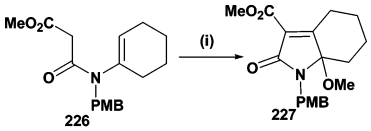
On the basis of the successful intramolecular cyclization of dicinnamyl ethers, leading to the synthesis of tetrahydrofurans such as **215 (**vide infra), other suitable cyclization

Table 6. Reaction of Homobenzylic Ethers with CAN[a]

Entry	Substrate	Product	Yield (%)
1			70
2			80
3			79
4			19

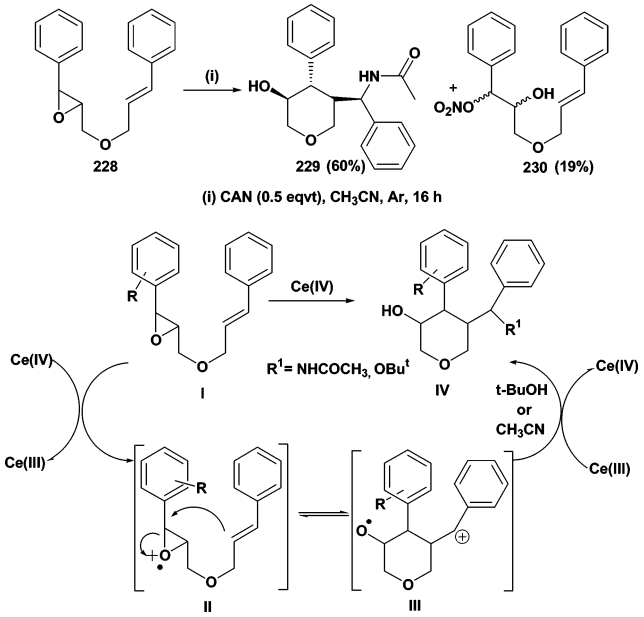
[a] Reaction conditions: CAN, $NaHCO_3$, 4 Å MS, CH_3CN, DCE.

Scheme 30



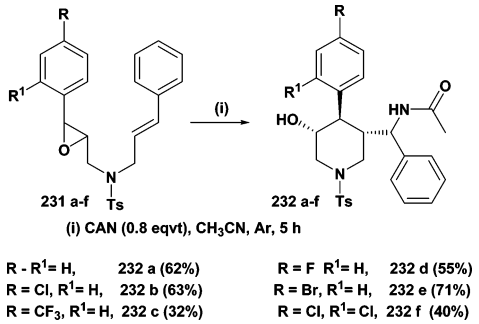
substrates were also developed. Epoxy cinnamyl ethers reacted in the presence of catalytic amounts of CAN leading to the synthesis of 3,4,5-trisubstituted tetrahydropyran derivatives in good yields (Scheme 31).[120] It is remarkable that

Scheme 31



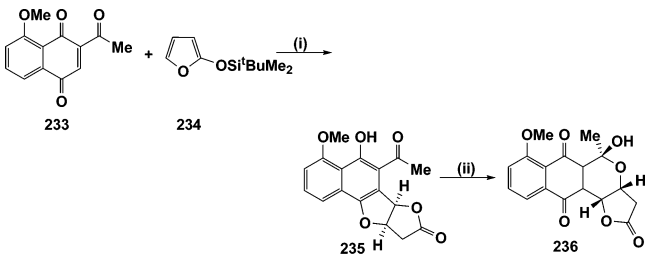
compound **229** was obtained stereoselectively: it has four contiguous stereocenters and some resemblance to the naturally occurring bioactive norlignans called sequirins. Mechanistic rationale regarding the reaction sequence starts with the oxidation of the epoxide moiety of ether **I** to the radical cation **II**. In less nucleophilic solvents, **II** exists in equilibrium with its distonic cyclic version **III**, whereas in nucleophilic solvents, solvolytic opening of **II** precludes cyclization. The incipient alkoxy radical in **III** gets reduced to the anion with concomitant reoxidation of Ce(III) to Ce(IV). The cationic center is then quenched by the solvent, affording the final product. On similar grounds, the stereoselective intramolecular cyclization of epoxypropyl cinnamyl amines mediated by CAN led to the synthesis of functionalized piperidines (Scheme 32).[121] The efficiency and stereoselectivity observed in the above reactions were utilized further for the synthesis of 3,4-trans-disubstituted pyrrolidines and cyclopentanes via intramolecular cyclization of *N*-cinnamyl *N*-tosyl-2-methoxycinnamyl amines and α-cinnamyl-α-(2-methoxycinnamyl)-malonates, respectively.[122]

Scheme 32



The efficiency of CAN in intramolecular cyclization was used by Brimble and co-workers recently for the synthesis of several pyranonaphthoquinone antibiotics, for example, kalafungin and their thia analogues.[123] **236** was formed by oxidative cyclization of the furonaphthofuran adduct **235**, which in turn was formed by conjugate addition of dimethyl *tert*-butyl silyloxyfuran **234** to the 1,4-quinone **233** (Scheme 33).

Scheme 33



3. Reactions Involving Carbon–Heteroatom Bond Formation

Carbon−heteroatom bond formation assumes much significance, especially from the vantage point of heterocyclic construction. The utility of CAN in carbon−heteroatom bond formation, particularly, C−S, C−N, C−Se, C−Br, and C−I bonds, is noteworthy in this connection. Mostly these reactions involve oxidative addition of heteroatom-centered radicals, formed by oxidation of anions by CAN, to alkenes or alkynes. Considering our recent review on this topic,[33] only selected literature along with later developments is covered in this section.

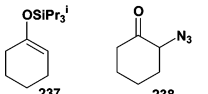
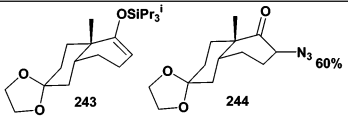
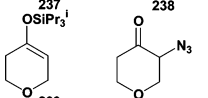
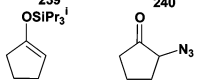
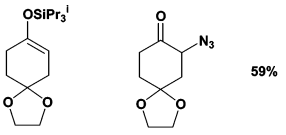
3.1. Carbon–Nitrogen Bond Formation

3.1.1. Introduction of Azide Functionality

Trahanovsky, in his seminal work which marks the beginning of the use of CAN for construction of carbon−heteroatom bonds, demonstrated that CAN promotes a facile addition of azide radicals to olefins like stilbene and acenaphthalene to afford *trans*-α-azido-*β*-nitratoalkanes.[124] Lemieux extended this protocol to the synthesis of azido sugars, which serve as convenient precursors of the corresponding amino sugars.[125] As azides are immediate precursors of amines, azidonitration strategy was also applied for the synthesis of amino acids.[126] CAN-mediated addition of azides to olefinic substrates like cinnamic acids, esters, and amides afforded the corresponding α-azido *β*-nitrato derivatives which on treatment with sodium acetate afforded vinyl azides, thus constituting a facile one-pot synthesis of the latter.[127]

Formation of α-azidoketones by oxidative azidation of silyl enol ether was reported first by Vogel during the total synthesis of deoxypolyoxin.[128] Magnus explored this reaction in detail employing triisopropyl silyl enol ethers as substrates since they are less prone to hydrolysis.[129] Oxidative azidation was applied to a range of cyclohexanone derivatives, affording the α-azidoketones in moderate to good yields. Selected examples are listed in Table 7.

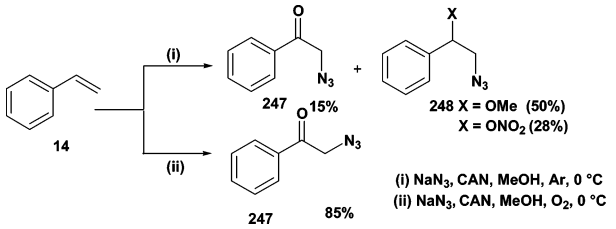
Table 7. Oxidative Azidation of TIPS Enol Ethers by CAN and NaN_3[a]

Substrate	Product	Yield	Substrate	Product	Yield
 237	238	72%	 243	244	60%
 239	240	47%			
 241	242	65%	 245	246	59%

[a] Reaction conditions: CAN, NaN_3, MeCN, −20 °C, argon.

In these reactions the solvent used was acetonitrile; however, work in our research group revealed a different reactivity in methanol. The azidomethyl ether was formed as the major product along with small amounts of the azido nitrate and azido ketone. In oxygen atmosphere, azido ketone was formed exclusively (Scheme 34).[130] Mechanistic details

Scheme 34

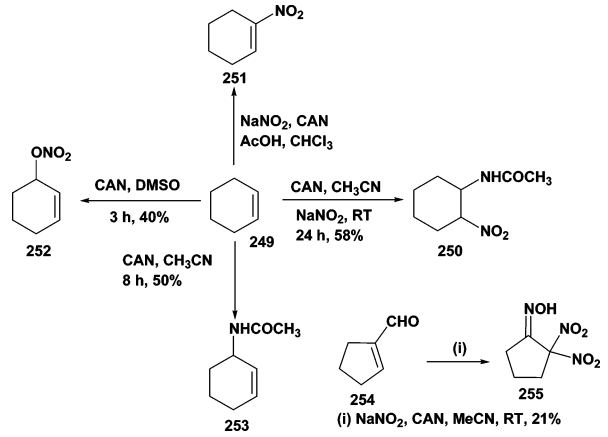


of this reaction have been described in our earlier review.[33]

3.1.2. Introduction of Nitro Functionality

Oxidation of cyclohexene by CAN in anhydrous DMSO led to formation of cyclohexene-3-nitrate, whereas in acetonitrile, *N*-(cyclohexene-2-yl) acetamide was formed.[131] Later, Hwu et al. reported that alkenes could be nitrated with excess sodium nitrite in the presence of CAN and acetic acid in chloroform.[132] He also showed that the same reagent combination can be used for the ultrasonic nitration of allylsilanes.[133] Simultaneous nitration and acetamidation was achieved in acetonitrile using CAN and sodium nitrite.[134] Evidently the acetamido product arises by quenching of the cationic intermediate by acetonitrile in a Ritter fashion followed by hydration of the iminium ion. Nitration of cyclohexene **249** under different conditions is illustrated in Scheme 35. Interestingly, attempted nitro acetamidation of

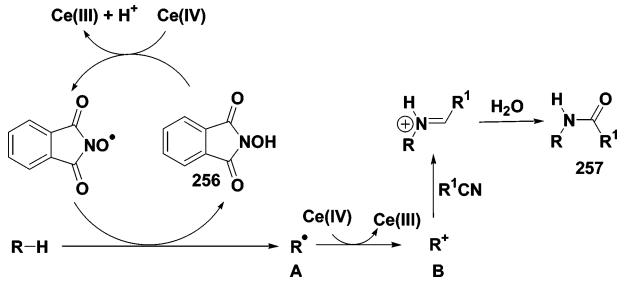
Scheme 35



cyclopentene carboxaldehyde **254** under similar reaction conditions resulted in formation of the unexpected dinitrooxime **255** (Scheme 35).[135]

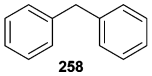
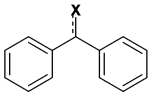
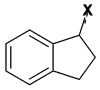
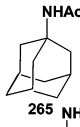
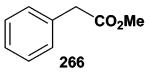
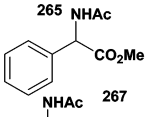
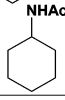
Ritter-type reaction of alkyl benzene with nitrile was reported using *N*-hydroxy-phthalimide (NHPI) **256** and CAN.[136] The reaction takes place by formation of the radical **A** from NHPI and CAN followed successively by hydrogen-atom abstraction and one-electron oxidation to form carbocation **B**. The latter is then trapped by nitrile followed by water to form amide derivative **257** (Scheme 36). Subsequent

Scheme 36



work in our research group has shown that CAN in combination with sodium azide can react with unactivated hydrocarbons in acetonitrile to furnish acetamides in good yields.[137] The reaction was found to be applicable for C−H oxidation of a variety of substrates; carboxylic esters afforded the corresponding amino acids. Mechanistically, product formation occurs by initial generation of the azido radical followed successively by benzylic hydrogen abstraction, oxidation of benzylic radical, and Ritter trapping with acetonitrile. The reaction represents a mild and simple protocol for C−H activation of hydrocarbons, which is very important in industry. Some of the results are presented in Table 8. A variety of aliphatic and aromatic nitriles were

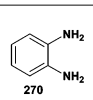
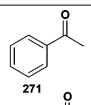
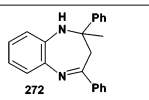
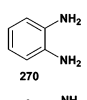
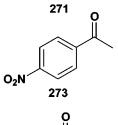
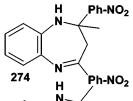
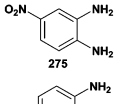
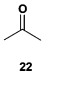
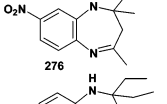
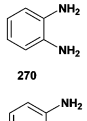
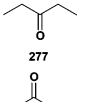
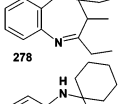
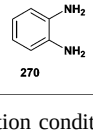
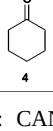
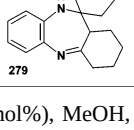
Table 8. C−H Activation Mediated by CAN and NaN_3[a]

Entry	Substrate	Product	Temp (°C)	Yield (%)
1	 258	 259 X = NHAc 260 X = O	70	259 = 58 260 = 20
2	 261	 262 X = NHAc 263 X = O	0	262 = 39 263 = 25
3	 264	 265 NHAc	30	85
4	 266	 267	70	30
5	 268	 269	70	16

[a] Reaction conditions: CAN (2.3 mmol), NaN_3, MeCN, Ar, 30 min.

prepared from the corresponding aldehydes using CAN and liquid ammonia in water under mild conditions.[138] CAN has also been used recently for the synthesis of conjugated nitro-olefins from α, β-unsaturated acids under mild conditions.[139] Another C−N bond-forming reaction, mediated by CAN, reported recently involves preparation of 1,5-benzodiazepine derivatives by reaction of substituted *o*-phenylenediamines and ketones.[140] It was observed that acetophenones containing halo substituents, except a bromo substituent, reacted rapidly to afford the corresponding benzodiazepines. Cyclic ketones such as cyclopentanone and cyclohexanone also reacted efficiently to afford the corresponding fused ring benzodiazepines in excellent yields. Some examples of this novel CAN-promoted 1,5-benzodiazepine synthesis are given in Table 9. The aza-Michael reaction of amines with α,β-

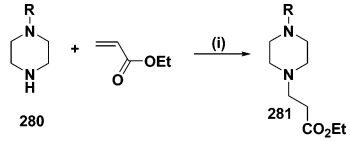
Table 9. Synthesis of 1,5-Benzodiazepines[a]

Entry	Diamine	Ketone	Benzodiazepine	Time (h)	Yield(%)
1	 270	 271	 272	3.5	89
2	 270	 273	 274	4.5	80
3	 275	 22	 276	3	92
4	 270	 277	 278	3	88
5	 270	 4	 279	3.5	98

[a] Reaction conditions: CAN (10 mol%), MeOH, RT.

unsaturated carbonyl compounds in water mediated by 3 mol % CAN led to formation of the corresponding β-amino carbonyl compounds in good to excellent yields (Scheme 37).[141]

Scheme 37



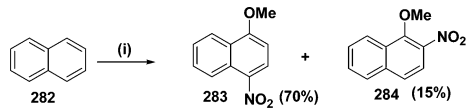
R = Ph, (10 min) 281 a (92%)
R = Me, (20 min) 281 b (70%)
R = CH_2Ph, (15 min) 281 c (88%)
R = H, (20 min) 281 d (80%)
R = Boc, (5 min) 281 e (92%)

(i) CAN (3 mol%), H_2O, RT

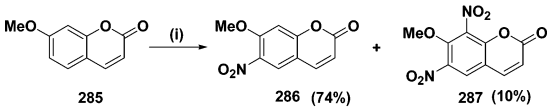
3.1.3. Nitration of Aromatic Nucleus

Silica-gel-supported CAN has been shown to nitrate polynuclear aromatic systems.[142,143] CAN-mediated nitration of naphthalene in the presence of catalytic amounts of sulfuric acid and *tert*-butylammonium nitrate in methanol afforded 1-nitro-4-methoxynaphthalene as the major product. The suggested mechanism for this reaction involves addition of the nitrite radical to naphthalene and oxidation of the resulting radical to cation followed by quenching with methanol.[143] 1-Naphthol reacted with CAN in acetic acid to afford dinitro compounds.[144] Mononitration occurred with electron-rich aromatic systems such as dimethoxy benzene.[145] Efficient mono- and dinitration of aromatic substrates was developed using CAN suspended in dichloromethane in the presence of two equivalents of sulfuric acid.[146] 6-Nitrocoumarin was reported to be the sole product formed by nitration of coumarin using one equivalent CAN in acetic acid. A minor amount of dinitro derivative was obtained with the presence of activating groups such as hydroxyl or methoxy on the phenyl ring.[147] *N*,*N*-Dialkyl anilines underwent regioselective nitration by CAN in acetonitrile to yield β-nitrated-*N*,*N*-dialkyl anilines in good yields.[148] Scheme 38 shows the nitration of naphthalene and methoxy coumarin.

Scheme 38



(i) CAN, $Bu_4N^+NO_2^-$, H_2SO_4, CH_3OH



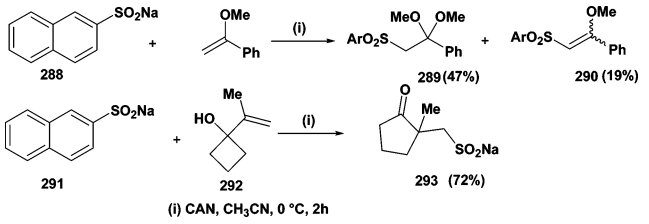
(i) CAN, 30% H_2O_2, H_2O

3.2. Carbon−Sulfur Bond Formation

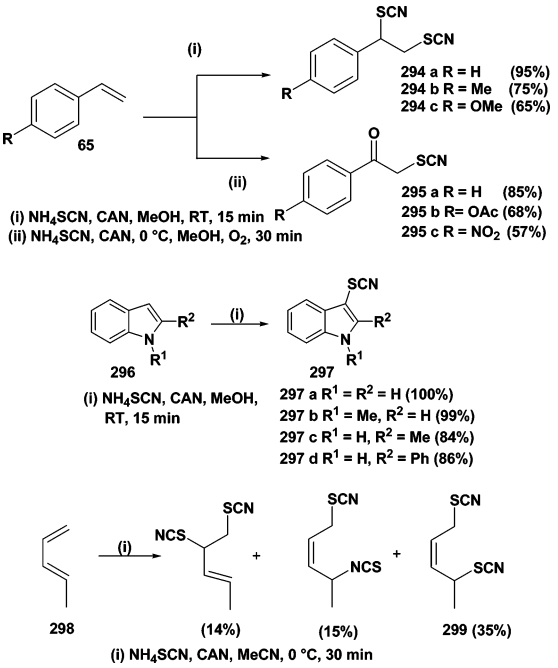
3.2.1. Sulfonylation

Sulfinates can be easily oxidized by CAN to generate sulfonyl radicals, which otherwise would require photolytic conditions or action of peroxides. Narasaka studied the addition of sulfinate to various olefins, especially electron-rich ones, in the presence of different one-electron oxidants such as manganese(III) 2-pyridine carboxylate [$Mn(pic)_3$], tetrabutylammonium cerium(IV) nitrate [TBACN], and CAN.[149] The reaction takes place by initial formation of a sulfonyl radical which adds to the olefin and subsequent oxidation. The same group also reported sulfonylation of 1-vinyl cyclic alcohols using CAN. Reaction of sodium-2-naphthalene sulfinate with 1-vinyl cyclobutanol **292** in acetonitrile resulting in formation of ring enlarged product **293** is illustrative (Scheme 39).[150] CAN-mediated oxidative

Scheme 39



Scheme 40



addition of sulfinates to styrenes has been shown to yield keto and nitrato sulfinates. Vinyl sulfones were formed as the sole product in the presence of sodium iodide, probably due to dehydroiodination of the intermediate iodovinyl sulfones.[151] Details of these reactions can be found in our earlier review.[33]

3.2.2. Thiocyanation

Thiocyanation of arenes and olefins constitutes an important method for introducing sulfur functionality. Reaction of styrene with ammonium thiocyanate and CAN afforded different products depending on the solvent employed. When the reaction was carried out in acetonitrile at ice bath temperature, dithiocyanates **294** were formed in excellent yield,[152] whereas in methanol, in an atmosphere saturated with oxygen phenacyl thiocyanate **295** was the predominant product (Scheme 40).[153] The same combination of reagents effected the thiocyanation of indoles, substituted indoles, pyrroles, and thiophenes (Scheme 40).[154] 1,3-Dienes on reaction with CAN and ammonium thiocyanate in acetonitrile afforded the corresponding 1,4-dithiocyanate and in some cases the dithiocyanates formed underwent a [3,3] sigmatropic rearrangement to afford the isothiocyanato-thiocyanates (Scheme 40).[154]

3.3. Carbon–Selenium Bond Formation

Introduction of the phenylseleno group into an organic molecule is of great synthetic importance. The common reagents for such transformations are phenylselenylbromide and phenylselenylchloride. Oxidation of diphenyldiselenide to the cation radical using CAN and subsequent trapping of the latter with olefins in methanol led to *p*-methoxyalkyl phenyl selenides in good yields.[155] Oxidative addition of selenocyanates to alkenes afforded diselenocyanates and keto selenocyanates.[156] The reaction could be forced in the desired direction to get either of the two products simply by changing the reaction conditions. In completely deoxygenated atmosphere, the diselenocyanate **301** was formed exclusively, whereas under oxygenated conditions, phenacyl selenocyanate **302** was formed as the sole product (Scheme 41).

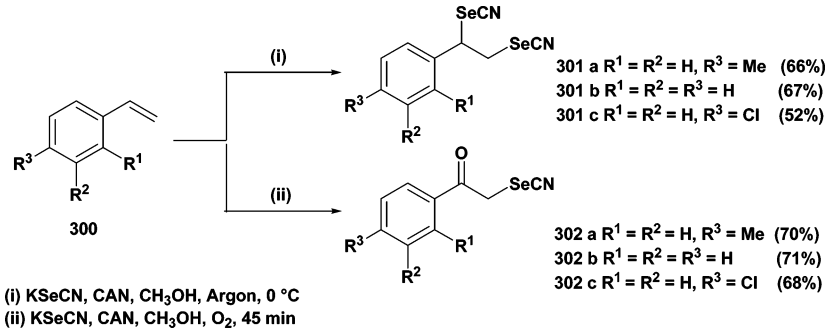
3.4. Carbon–Halogen Bond Formation

CAN functions as an excellent reagent for carbon−halogen bond formation. A number of reactions are reported in the literature pertaining to this aspect of CAN chemistry.

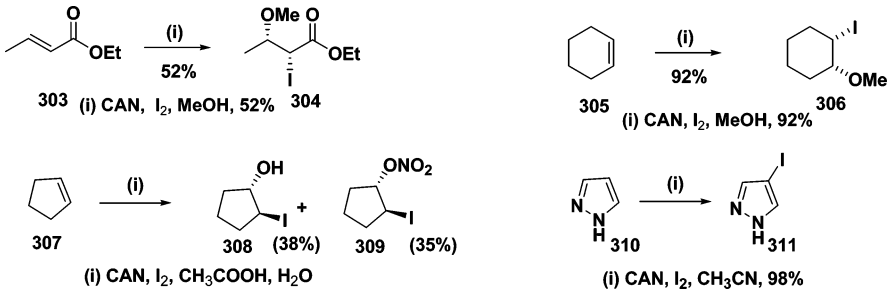
3.4.1. Iodination

Regioselective iodination of an aromatic nucleus has been achieved using CAN and an iodide-like tetrabutylammonium iodide, alkali-metal iodide, or molecular iodine.[157] Horiuchi et al. reported the facile α-iodination and α,α′-iodination of ketones using a combination of iodine and CAN in solvents such as acetic acid and methanol.[158,159] Reaction of α,*β*-unsaturated ketones and esters with iodine and CAN in methanol, ethanol, or isopropyl alcohol, under reflux conditions afforded the corresponding *β*-alkoxy α-iodo-ketones and esters in very good yields (Scheme 42).[160] When the solvent was acetonitrile, *β*-hydroxy α-iodo-ketones and esters were obtained.[160] Horiuchi also described the reaction of 2-cyclohexen-1-one with I_2−CAN in alcohol under reflux condition leading to the corresponding alkyl phenyl ethers in good yields.[161] Under the same reaction conditions, isophorone (3,5,5-trimethyl cyclohex-2-ene-1-one) was found to undergo oxidative rearrangement with 1,2-migration of the C_5-methyl group. Cycloalkenes on treatment with iodine and CAN in alcohols such as methanol, ethanol, 1-propanol, or 2-propanol under reflux conditions gave the corresponding

Scheme 41



Scheme 42

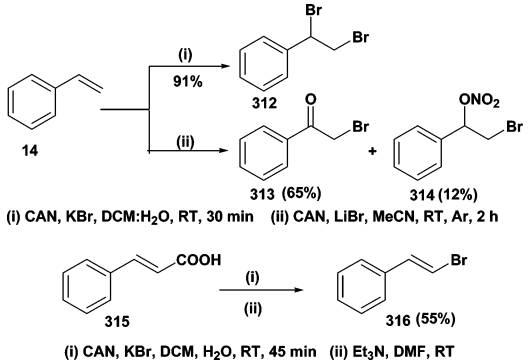


vicinal alkoxyiodo cycloalkanes.[162,163] When the solvent was *tert*-butyl alcohol, the product was *trans*-iodonitrate.[162] Cycloalkenes on treatment with iodine and CAN in acetonitrile-water afforded the corresponding *trans*-iodohydrins and *trans*-iodonitrates.[164] 3-Iodo derivatives of flavones, thioflavones, and thiochromones were prepared by reaction of benzopyran and benzothiopyran with CAN and iodine.[165] Asakura et al. reported iodination of C-5 of uracil nucleosides using catalytic amounts of CAN in acetonitrile or DMF.[166] An expeditious and stereoselective synthesis of 2-deoxy-2-iodo-α-manno-pyranosyl acetates by the CAN-mediated addition of iodide to glycals has been reported recently by Roush et al.[167] Regioselective iodination of pyrazoles using elemental iodine in the presence of CAN constitutes a mild and efficient method for preparation of 4-iodopyrazoles.[168] Scheme 42 depicts some typical iodination reactions mediated by CAN.

3.4.2. Bromination

Alkyl aromatics were brominated in the side chain using sodium bromide and CAN.[169] Asakura et al. reported bromination of C-5 of uracil nucleosides using CAN and lithium bromide in acetonitrile.[170] Work in our research group has shown that alkenes can be converted to the dibromides using potassium bromide and CAN in a two-phase system of water and dichloromethane. When the solvent used was methanol, acetonitrile, or acetic acid, phenacyl bromide **313** and nitrato bromide **314** were formed (Scheme 43).[171]

Scheme 43

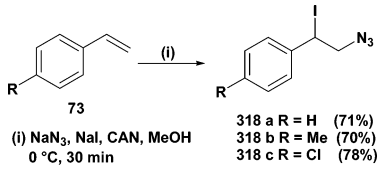


Cinnamic acid **315** was efficiently converted to β-bromostyrene **316** by the reagent combination of CAN and potassium bromide (Scheme 43). In addition, selective bromoalkoxylation of activated cinnamyl systems was achieved using lithium bromide and propargyl alcohol in the presence of CAN.[172]

3.4.3. Azidoiodination and Iodothiocyanation

Bis-functionalization of double bonds, in particular co-halogenation of olefins, constitutes a very useful organic transformation. CAN-mediated azidoiodination offers the most convenient protocol due to the experimental simplicity. A one-pot double functionalization of alkenes to azidoiodides by use of NaI, NaN_3, and CAN has been reported (Scheme 44).[173] The reaction was found to be applicable to a number

Scheme 44



of alkenes. Styrene yielded iodothiocyanate and phenacyl thiocyanate on treatment with ammonium thiocyanate, sodium iodide, and CAN in methanol at ice bath temperature. With cyclohexene and octene, the corresponding iodothiocyanate was the only product.

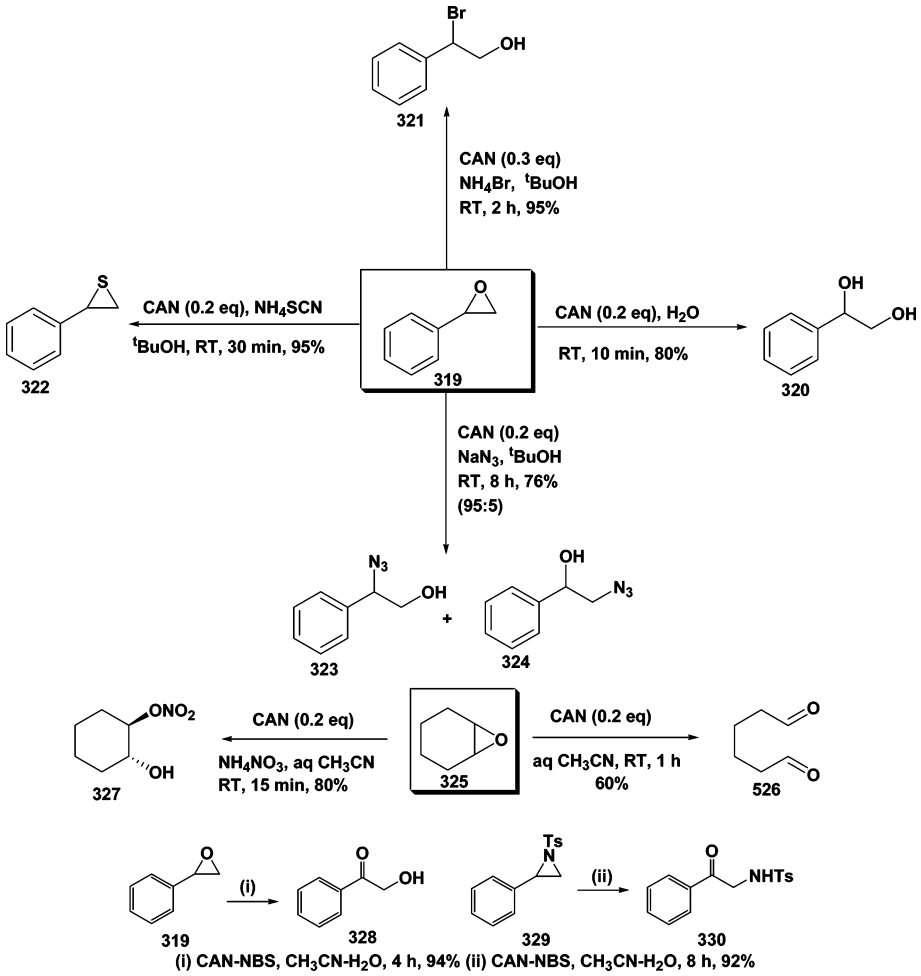
4. Reactions Involving CAN as a Catalytic Oxidant

Although CAN is far superior to many other one-electron oxidants, the vast majority of CAN-mediated oxidations require more than two equivalents of the oxidant for completion of the reaction. This precludes its use in large-scale transformations. Development of reactions requiring only catalytic amounts of CAN is therefore very important. Some of these reactions are illustrated here.

4.1. Oxidative Transformations of Epoxides

The study of CAN-mediated oxidative transformations of epoxides has been pursued in detail. Ring opening of epoxides was accomplished using CAN under different conditions (Scheme 45). Regioselective ring opening was effected by employing CAN in the presence of alcohols, water, thiols, and acetic acid.[174] Direct oxidative cleavage of epoxides to the corresponding dicarbonyl compounds was reported using CAN in aqueous acetonitrile.[175] Synthesis of β-halohydrins such as **321** by the CAN-mediated regio- and stereoselective ring opening of epoxides in the presence of ammonium salts has also been reported.[176] Epoxides were converted to the corresponding β-nitrato alcohols **327** by treatment with catalytic amounts of CAN in the presence of excess nitrate ions, present as the ammonium or tetra-*n*-butyl ammonium salt.[177] Fabio and co-workers utilized the above strategy for the preparation of various 4-alkoxy-substituted trinems, novel tricyclic β-lactam derivatives endowed with outstanding chemical and metabolic activity.[178] Cleavage of unhindered steroidal epoxides by CAN also afforded the trans diaxial β-nitrato alcohols.[179] 1,2-Azidoalcohols **323** and **324** were prepared in good yields by regioselective ring opening

Scheme 45



of epoxides in the presence of sodium azide and catalytic amounts of CAN.[180] Efficient conversion of various epoxides to the corresponding thiiranes, **322** for instance, was reported in the presence of ammonium thiocyanate and catalytic amounts of CAN.[181] The various transformations of CAN reported above are summarized in Scheme 45, taking styrene epoxide as a representative substrate. Similar to the ring-opening reactions of epoxides, cleavage of *N*-tosyl aziridines to afford vicinal azidoamines has also been reported. With other nucleophiles such as water and methanol the corresponding vicinal aminols and amino ethers were obtained.[182] Like epoxides, a facile CAN-mediated oxidative rearrangement of oxetanes was also reported.[183] *N*-Tosyl aziridines were reported to undergo ring opening with water in the presence of catalytic amounts of CAN to furnish the corresponding amino alcohols in good yields.[184] Ring opening of epoxides and aziridines to the corresponding α-hydroxy or α-amino ketones **328** and **330** was achieved using CAN and NBS (Scheme 45). The reaction is probably initiated by hydrolysis of the substrate by CAN followed by oxidation with NBS to give the corresponding keto product.[185]

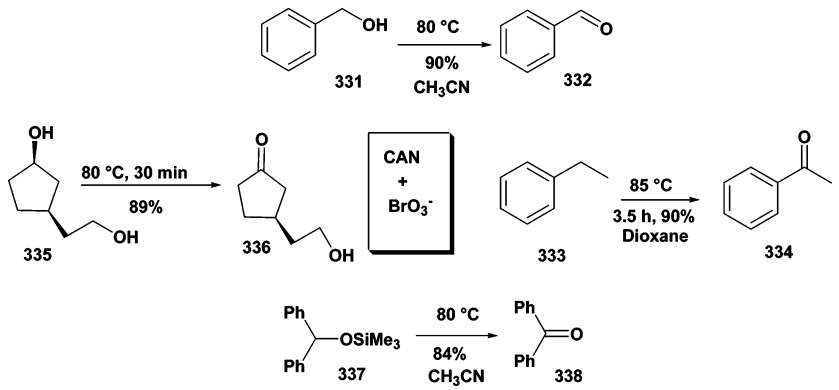
4.2. CAN-Bromate Oxidations

Apart from the catalytic use of CAN in reactions involving epoxides there are also reports on the catalytic use of CAN in oxidations with bromate ion serving as the co-oxidant. Oxidation of benzyl alcohol **331** to benzaldehyde **332** in the presence of CAN and sodium bromate is the first report on this type of reaction.[186] Many years later, oxidation of alkyl aromatic compounds to ketones such as **334** in the presence of CAN and potassium bromate was reported.[187] Oxidative cleavage of alkyl ethers and trialkyl silyl ethers **337** was effected with CAN and sodium bromate.[188] CAN−bromate reagent combination also promoted the selective oxidation of secondary alcohol **335** in the presence of primary ones.[189] Scheme 46 summarizes the versatility of CAN−bromate reactions. Additionally, CAN has also been used as an effective catalyst for esterification of carboxylic acids and alcohols including steroids and other multifunctional compounds under mild reaction conditions.[190] 2-Methoxyethoxymethyl ethers were readily cleaved by catalytic amounts of CAN in acetic anhydride to afford mixed acetal esters.[191] CAN in catalytic amounts also facilitated hydrolysis of peptides.[192]

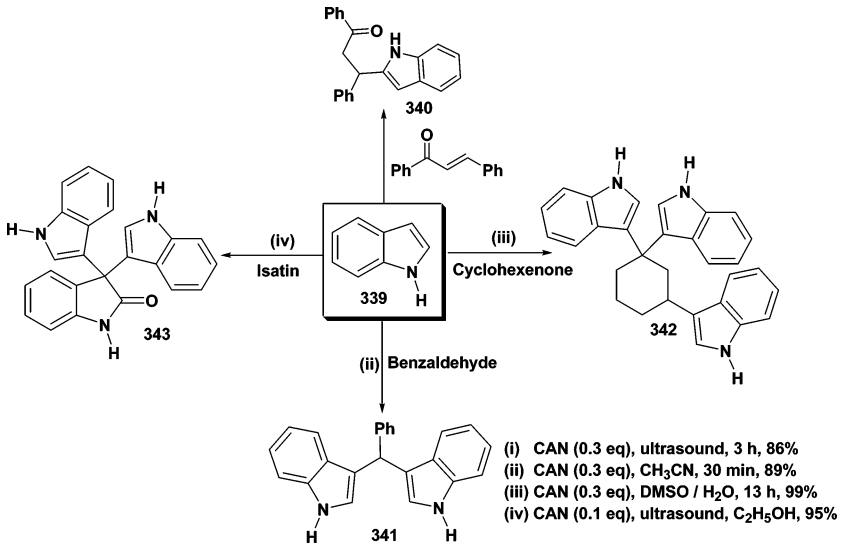
4.3. Electrophilic Substitution Reactions of Indoles

Recently CAN was found to be an efficient catalyst for the electrophilic substitution reaction of indoles with carbonyl compounds resulting in formation of di- and tri-indolylmethanes in high yields.[193] Instead of playing its usual role of a single-electron oxidant, here CAN serves as a Lewis acid. It activates the carbonyl group by coordinating to the lone pair of electrons of oxygen so that bond formation at C-3 of indoles with the carbonyl group is favored. Michael addition of indole to α, β-unsaturated ketones under ultrasonic irradiation afforded the corresponding adduct **340** in excellent yield.[194] 1,2-Addition products of indole **339** were

Scheme 46



Scheme 47



reported by reaction of indole with α, *β*-unsaturated ketones or aldehydes in the presence of 0.3 equiv of CAN.[195] CAN-catalyzed reaction of isatin with indole under sonic waves lead to formation of symmetrical 3,3-(indolyl)indolin-2-one **343**.[196] Scheme 47 summarizes the reported results in this area.

4.4. Imino-Diels–Alder Reactions

Recently, a CAN-catalyzed imino-Diels−Alder reaction between aryl imines and *N*-methyl-*N*-vinyl acetamide leading to stereoselective formation of the corresponding 2,4-*cis*-4-amido-*N*-methyl tetrahydroquinoline derivative in good yields was reported.[197] The reaction occurs by preferential oxidation of the amide **345** over the imine **344**, the latter having a lower oxidation potential compared to the former. The terminal carbon of the intermediate **I** then adds regioselectively to the imine, forming the cation radical **II**, which subsequently undergoes ring closure followed by 1,3-hydrogen shift and gets reduced to give the final product (Scheme 48). Simultaneously, synthesis of other heteroaryl-substituted tetrahydroquinolines and their oxidation to the corresponding heteroaryl-substituted quinolines was reported using catalytic amounts of CAN in aqueous medium.[198]

5. Deprotection–Protection Sequences Mediated by CAN

The most frequently encountered functional group transformation in organic synthesis is the protection−deprotection sequence. This is testified by the plethora of reagents and methods of general and/or specific utility that have been devised to accomplish such transformations. In recent years CAN has also proved to be an effective reagent for these transformations. Some of the protection−deprotection sequences mediated by CAN are described in this section.

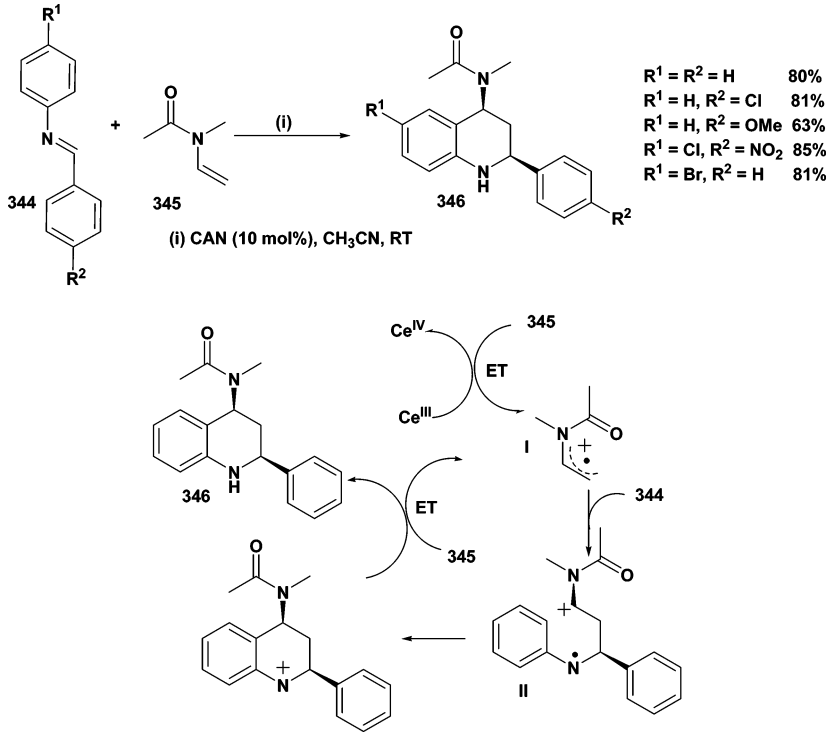
5.1. Earlier Reports

Oxidative cleavage of both σ and π complexes incorporating organometallic moieties by treatment with CAN has been reported (Scheme 49). Ligands like cyclobutadiene[199−202] and methylene-γ-butyrolactone[203] have been liberated successfully for their participation in synthetic transformations. In the recovery of organic products from a Dötz reaction, CAN is often employed to cleave off the metallic species as in the reaction of **349**.[204]

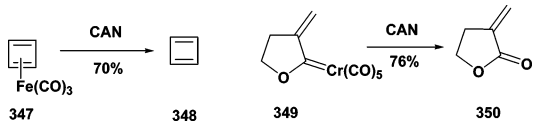
Early work has shown that CAN is an effective reagent for deprotection of carbonyl protecting groups. Oximes and semicarbazones were oxidized to the parent carbonyl compound by CAN in ethanol.[205] In 1972, Ho et al. showed that dithioacetals such as **351** can be unmasked to the parent carbonyl compound by employing CAN in aqueous acetonitrile.[206] In a series of compounds in which the dithiolane group was sterically hindered, the reaction led to enones, i.e., dehydrogenation accompanied the deprotection. An illustrative example of formation of **354** is depicted in Scheme 50.

Another reaction that is very useful in the preparation of quinones involves oxidative demethylation by CAN. Cat-

Scheme 48



Scheme 49



echols, hydroquinones, and their methyl ethers can readily afford quinones by CAN oxidation.[207] Tetramethoxy naphthalene **355** underwent oxidative demethylation with CAN giving rise to two isomeric dimethoxy naphthoquinones **356** and **357** as depicted in Scheme 51.[208] Partial demethylation oxidation was also feasible as shown in the preparation of several quinhydrones **359**.[209] In a synthesis of methoxatin, the *o*-quinone moiety was generated from the aryl methyl ether **360**.[210] Demethylation strategy by CAN was applied for the preparation of cyclopropanaphthoquinone, the first stable cyclopropaquinone reported.[211] Synthesis of benzo[*b*]thiophene-4,7-quinones was achieved by the demethylation reaction of 4,7-dimethoxybenzo[*b*]thiophenes in the presence of CAN in acetonitrile−water solution.[212]

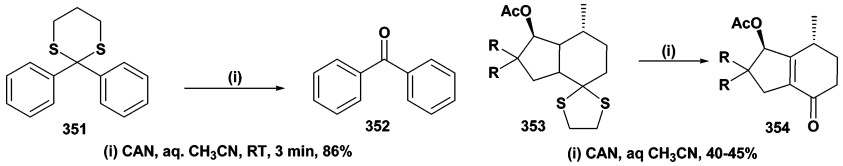
5.2. Deprotection of Acetals

Acetals and ketals enjoy an important position among the variety of groups employed for carbonyl protection. This is attested by the numerous and diverse methods devised for their attachment and removal. Unfortunately all these methods required strongly acidic conditions and were not suitable for sensitive substrates. Here again, CAN acts as a mild reagent to deprotect the acetal moiety. One of the early reports in this area is on the deprotection of benzaldehyde diacetates to the corresponding benzaldehydes using CAN coated on silica in dichloromethane.[213] The authors observed that deprotection occurred selectively on 4-acetoxybenzaldehyde diacetates **b** and **c** without cleavage of the phenolic acetate (Scheme 52).

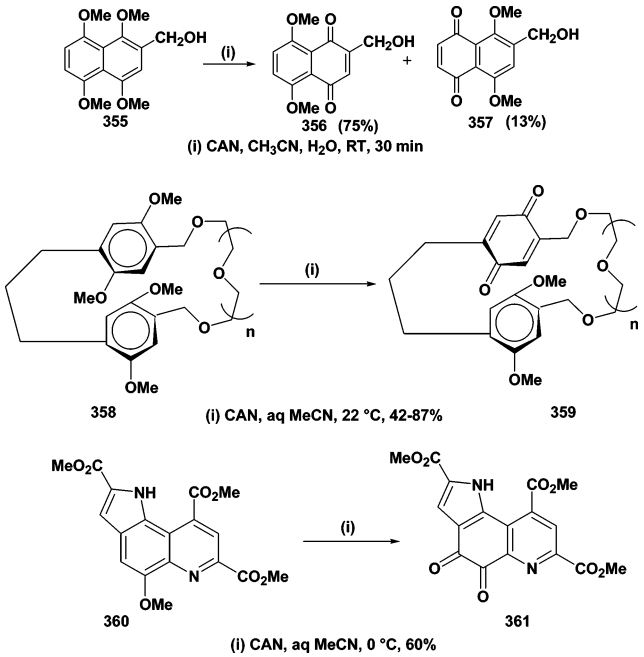
An unusually mild and efficient method for deprotection of acetals was developed by our research group employing 1.2 equiv of CAN in aqueous methanol.[214] Mechanistically, the reaction is probably initiated by removal of an electron from the acetal to give the radical cation **A**. Fragmentation of **A** to the distonic species **B**, in accordance with the known reactions of radical cations, is not surprising. Abstraction of hydrogen by **B** followed by addition of water can give rise to the hemiacetal **D**, and the latter can suffer fragmentation to generate the carbonyl compound. The possibility that the deprotection of acetal is brought about by the acid generated from CAN may be ruled out since the deprotection occurs equally well in the presence of excess $NaHCO_3$ or Na_2CO_3 also. Some examples are shown in Table 10, and the mechanism is depicted in Scheme 53.

Simultaneously, Marko et al. also developed two CAN-mediated procedures for deprotection of acetals. Initially they employed 2.5 equiv of CAN in aqueous acetonitrile for deprotection and demonstrated that the reaction is not an acid-catalyzed process, as deprotection was achieved under basic conditions in the presence of K_2CO_3 also.[215] Observing the unsuitability of the procedure to sensitive substrates and requirement for a large quantity of CAN for the process,

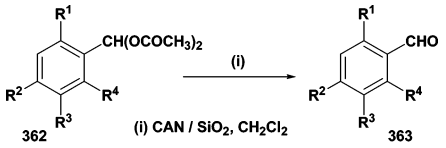
Scheme 50



Scheme 51

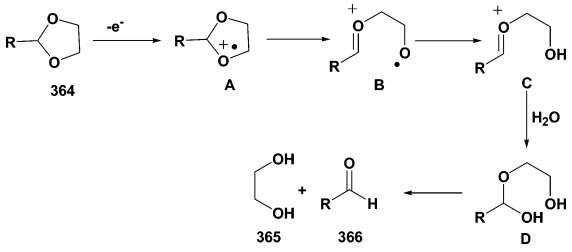


Scheme 52



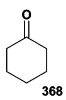
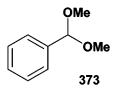
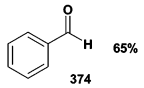
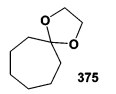
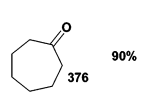
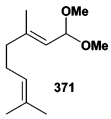
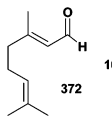
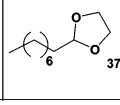
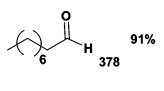
	R^1	R^2	R^3	R^4	Yield(%)
a	OMe	H	OMe	H	92
b	H	OCOMe	H	H	98
c	H	OCOMe	OMe	H	90
d	OMe	NO_2	OMe	H	94
e	OMe	H	OMe	NO_2	95

Scheme 53



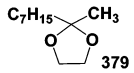
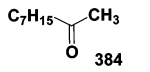
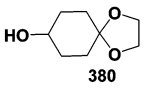
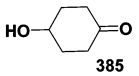
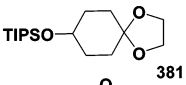
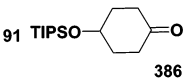
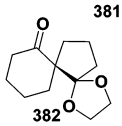
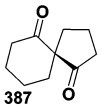
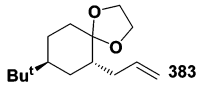
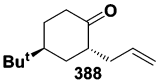
the same group developed another method for the deprotection. They found that catalytic amounts of CAN in the presence of borate−HCl buffer (pH 8) accomplished the deprotection effectively.[216] A variety of cyclic ketals and acetals can be deprotected using this strategy, and the reaction tolerates a range of functional groups. The authors monitored the deprotection reaction by cyclic voltammetry in which they could detect only the Ce^{IV} species. Hence, they surmise that in this reaction CAN acts as a highly selective and efficient Lewis acid that activates the acetal or ketal protecting groups toward hydrolysis and not as a redox agent. Table 11 summarizes some of these results. Marko et al.

Table 10. Deprotection of Acetals with CAN in Aqueous Methanol[a]

Substrate	Product	Yield	Substrate	Product	Yield
 367	 368	84%	 373	 374	65%
 369	 370	80%	 375	 376	90%
 371	 372	100%	 377	 378	91%

[a] Reaction conditions: CAN (1.2 equiv), aq MeOH, RT, 10 min.

Table 11. Deprotection of Acetals with CAN in Borate·HCl Buffer[a]

Entry	Sunstrate	Time	Yield (%)	Product
1	 379	30 min	95	 384
2	 380	25 min	92	 385
3	 381	45 min	91	 386
4	 382	1.5 h	86	 387
5	 383	20 min	96	 388

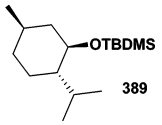
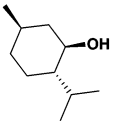
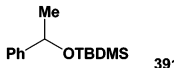
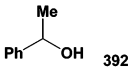
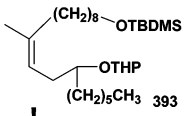
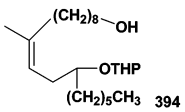
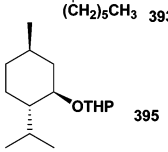
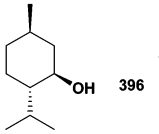
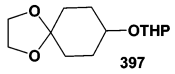
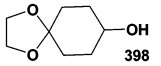
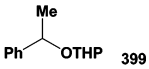
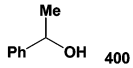
[a] Reaction conditions: CAN (3 mol%), borate-HCl buffer (pH 8).

also reported that dioxolane ketals derived from both cyclic and acyclic ketones containing a enol−triflate moiety could be smoothly deprotected without hydrolysis of the triflate function using 3 mol % CAN leading to formation of monoenol diketones. Using this mild procedure, ketals, THP ethers, and TBDMS ethers were chemoselectively and efficiently unmasked without affecting the acid-labile enol triflate functionality.[217]

5.3. Removal of TBDMS, THP, and *t*-BOC Groups

Protection of alcohols as TBDMS ether is very well established in organic synthesis because of its easy installation and general stability to basic and mild acidic reagents. Deprotection of TBDMS ethers is usually done with aqueous acids, fluoride ion, and aqueous HF−CH_3CN. Singh and coworkers accomplished cleavage of TBDMS ethers using CAN in methanol.[218] The reaction was found to be applicable to a number of TBDMS ethers with different steric and electronic environments. Some of the results are tabulated in Table 12. It was found that selective cleavage of primary TBDMS ether over secondary THP ether was possible (entry 3). They also observed that deprotection of THP ethers could be achieved using CAN in methanol at 0 °C. Entries 4−6 of Table 12 show the THP ether cleavage. The authors postulate that an activated complex formed from methanol

Table 12. Deprotection of TBDMS and THP Groups with CAN in Methanol[a]

Entry	Substrate	Time	Product	Yield (%)
1	 389	2.5 h	 390	95
2	 391	1.5 h	 392	86
3	 393	15 min	 394	95
4	 395	30 min	 396	90
5	 397	1.5 h	 398	90
6	 399	3 h	 400	81

[a] Reaction conditions: CAN (3 mol %), MeCN/borate buffer.

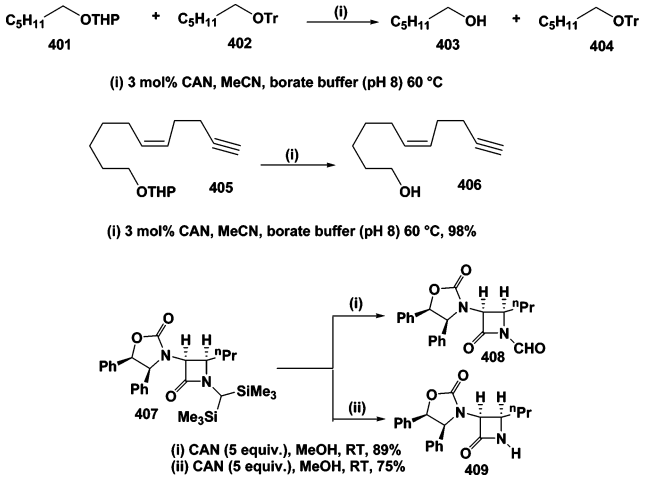
and CAN is responsible for the deprotection reactions, as it is known from the literature that a 1:1 red-colored complex is formed by CAN with alcohols. Attack of the methanol of the activated complex on the silicon group is facilitated by coordination of Ce(IV) with oxygen. Marko et al. also described a CAN-catalyzed protocol for removal of THP ethers under neutral conditions employing 3 mol % CAN in aqueous acetonitrile and borate buffer (pH 8). Here again, the Lewis acidity of CAN is invoked to explain the mechanism. Good selectivity was observed in the presence of other protecting groups, which allowed selective deprotection of a THP group in the presence of a trityloxy substituent (Scheme 54).[219] The ability of CAN to cleave the C−Si bond was utilized for removal of the *N*-[bis-(trimethylsilyl)methyl] moiety from the β-lactam **407**.[220] Treatment of the latter with CAN in acetonitrile afforded the aldehyde **408**, while on prolonged exposure of **407** to CAN in methanol at room-temperature unsubstituted β-lactam **409** was obtained (Scheme 54).

Deprotection of the *t*-BOC group from organic compounds under neutral conditions was achieved using catalytic amounts of CAN in acetonitrile.[221] Mechanistically, removal of the *t*-BOC group occurs by initial oxidation of the carbonyl group in **I** to the corresponding radical cation **II**; the latter then undergoes fragmentation to give the *tert*-butyl cation **III** and carboxylate radical **IV**. Regeneration of Ce(IV) from Ce(III) during reduction of carboxylate radical **IV** to carboxylate ion **V** allowed use of CAN in catalytic amounts for the entire deprotection. The final step was extrusion of carbon dioxide from **V** followed by protonation to give the free amine **VI**. An illustrative example for the deprotection and a general mechanistic rationale is given in Scheme 55.

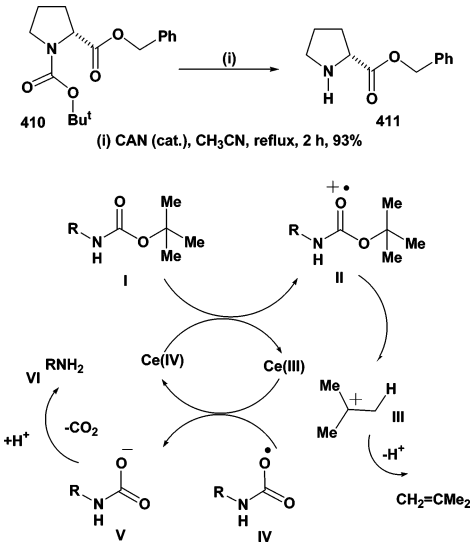
5.4. Removal of Trityl and Silyl Groups

Trityl and monomethoxytrityl groups could be efficiently removed from protected nucleosides or nucleotides by

Scheme 54



Scheme 55

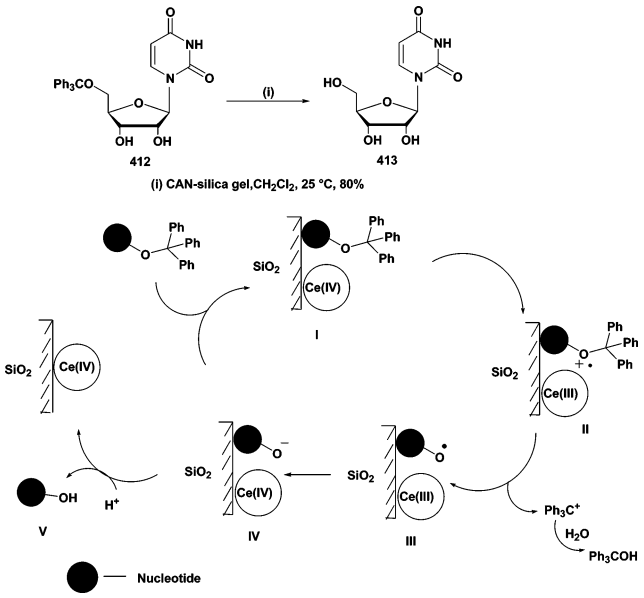


catalytic amounts of CAN in wet acetonitrile in DMF under neutral conditions.[222] Absorption of organic compounds containing trityl or silyl groups onto CAN−SiO_2 reagent is known to facilitate electron-transfer process and causes deprotection to proceed much faster.[223−226] The strategy of absorption on silica was also efficiently employed for the selective cleavage of trityl, monomethoxytrityl (MMTr), and dimethoxytrityl (DMTr) groups from protected nucleotides and nucleosides under mild conditions.[227] A generalized mechanistic interpretation and illustrative examples are shown in Scheme 56. The trityl-containing compounds get absorbed on silica to afford **I**, which then undergoes oxidation to give the radical cation **II**. The same mechanism operates for desilylation also.

5.5. Removal of Benzyl, PMB, and PMPE Groups

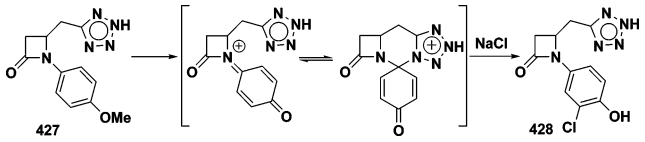
Treatment of tertiary amines such as **414** with one or more *N*-benzyl protecting groups with aqueous CAN resulted in clean debenzylation to afford the corresponding secondary amines (Scheme 57).[228,229] The debenzylation strategy was applicable to a number of tertiary amines, and in all cases the reaction was found to be chemoselective. The protocol was employed for the solid-phase synthesis of secondary amines. Some examples for the debenzylation and solid-phase synthesis of dihexylamine from **418** are depicted in

Scheme 56



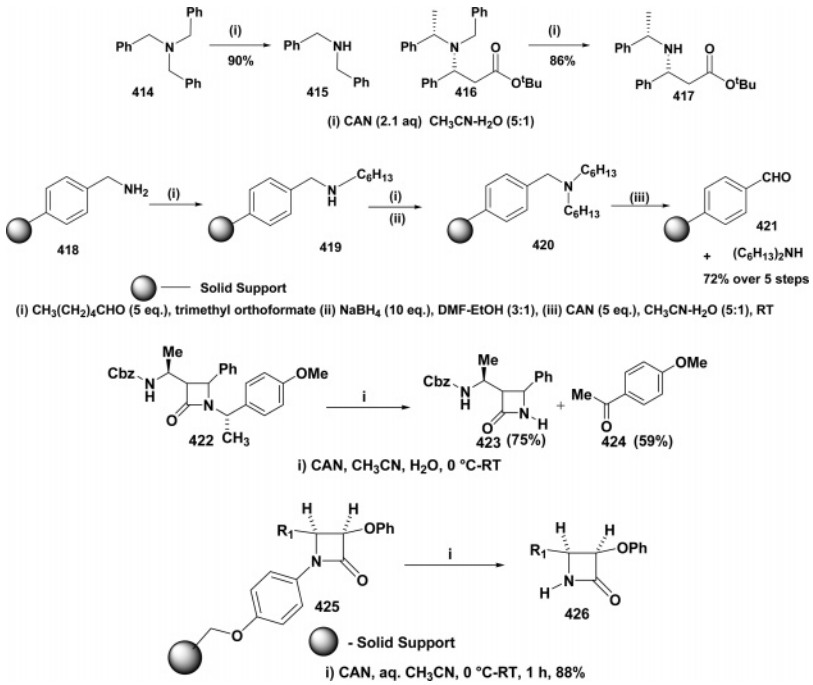
Scheme 57. Selective cleavage of the PMB (4-methoxybenzyl) group in the presence of the NAP (2-naphthylmethyl) group was achieved using CAN with a range of monosaccharides.[230] Easy removal of the PMPE group by CAN was utilized for the synthesis of β-amino acid derivatives.[231] CAN has also been used for deprotection of *p*-methoxyphenethyl (PMPE) groups. Removal of the *p*-methoxyphenethyl group from β-lactam **422** was achieved using CAN in acetonitrile.[232] Tomioka et al. reported a CAN-mediated oxidative removal of the *N*-PMP group.[233] β-Lactams substituted at the amide nitrogen with a benzyloxy aniline linker **425** when treated with CAN underwent a facile oxidative cleavage of the benzyloxy group to afford the deprotected *N*-unsubstituted β-lactam **426** in good yield.[234] Attempted deprotection of the *p*-methoxyphenyl group from the β-lactam containing a tetrazol-5-ylmethyl tether resulted in formation of a product containing a modified substituent attached to the ring nitrogen atom.[235] The product formation can be rationalized by assuming an interaction between the nucleophilic tetrazole and electrophilic quinoneimine moiety; the latter is formed by CAN oxidation of the initial substrate (Scheme 58).

Scheme 58

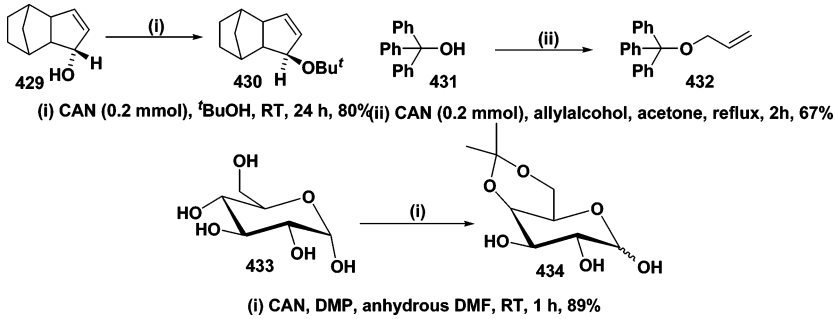


In comparison to the deprotection sequences, there are only few reports on the protection sequences mediated by CAN. Iranpoor has shown that catalytic amounts of CAN would effect the conversion of allylic and tertiary benzylic alcohols **429** and **431** into their corresponding ethers **430** and **432** in appropriate alcohols (Scheme 59).[236] The wide spectrum of the reactivity of CAN was exemplified by its use in acetalization reactions as well. Acetonation of carbohydrates using 2,2-dimethoxypropane took place in the presence of CAN in anhydrous DMF as solvent.[237] CAN-catalyzed tetrahydropyranylation of alcohols and synthesis of 2-deoxy-*O*-glycosides were reported by Vankar.[238] It was found that a variety of alcohols reacted with 2 equiv of dihydropyran in the presence of catalytic amounts of CAN in acetonitrile to form the corresponding THP ethers in good to excellent yields. Glycals **437** and **438** underwent addition of alcohols to form the corresponding 2-deoxy-*O*-glycosides **439** and **440**, respectively (Scheme 60). An efficient method for the preparation of dimethyl, diethyl, and diallyl acetals of aromatic aldehydes mediated by CAN was reported using the corresponding alcohols as the solvent.[239] Recently a monoprotection reaction of the glycol moiety as in **441** in the presence of catalytic amounts of CAN was reported by Rodriguez et al.[240] The reaction proceeds via an orthoester intermediate and was found to be highly selective in the presence of a heteroatom adjacent to the glycol functionality (Scheme 60). Very recently, a chemoselective solvent-free

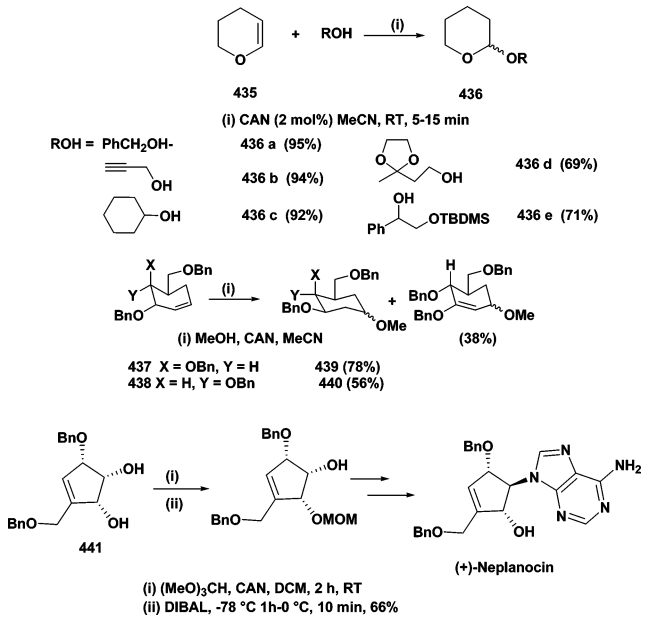
Scheme 57



Scheme 59



Scheme 60



method for the synthesis of acylals and their deprotection to 4-oxo-4*H*-1-benzopyran-3-carbaldehyde catalyzed by CAN was reported.[241]

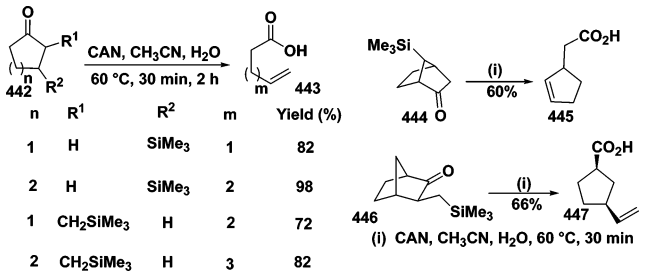
6. Miscellaneous Transformations

In addition to the reactions described above, CAN has also been effective in bringing about some novel and interesting processes. Such reactions also provide insight into the mechanistic details of several CAN-mediated transformations. A few illustrative examples are cited in this section.

6.1. Fragmentation Reactions

Oxidative fragmentation reactions mediated by CAN were reported as early as 1966 by Trahanovsky.[39] Cycloalkanones underwent an oxidative fragmentation with CAN in acetonitrile to afford 6- and 5-nitrato carboxylic acids in a ratio of 3:2.[242] Oxidative fragmentation of steroidal alcohols was accomplished in the presence of CAN in aqueous acetonitrile.[243] Recently the diol cleavage reaction was applied for the synthesis of β-amino carbonyl compounds by the CAN-mediated oxidative cleavage of 4-aryl-3,4-dihydropiperidines.[244] Oxidative fragmentation of organic compounds containing the trimethyl silyl moiety was also extensively investigated. Trahanovsky reported that γ-hydroxy silanes undergo oxidative fragmentation by CAN to yield aldehydes.[245] Wilson et al. extended the same reaction to cyclic substrates, resulting in formation of ketones.[246] Hwu and co-workers reported a highly regioselective, silicon-directed C−C bond cleavage of β-(trimethylsilyl)cycloalkanones **442** to afford ω-alkenyl carboxylic acids **443** in the presence of CAN.[247] The reaction was applicable to five- and six-membered cycloalkanones bearing a β-silyl group at the endo or exo position. The presence of the silyl group at the β position plays a profound role in stabilizing the intermediate carbocations and carboradicals. Scheme 61 illustrates some

Scheme 61



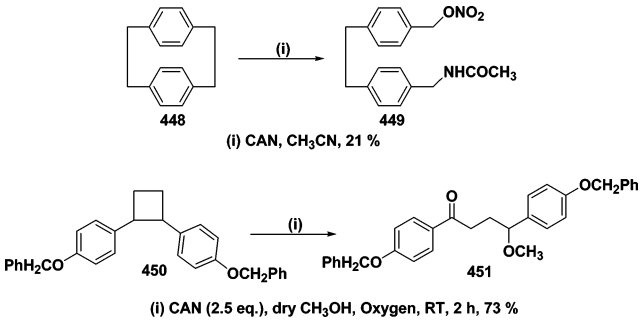
of the desilylation reactions mediated by CAN.

CAN-mediated cleavage of [2.2] paracyclophane resulted in generation of a double benzylic radical cation which is trapped by various nucleophiles to generate products such as **449**.[248] Several CAN-mediated ring-opening reactions of cyclopropanes are also known in the literature. Reaction of phenyl and diphenyl cyclopropane with CAN in acetic acid and acetonitrile has been studied by Young.[249] 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.[250] A detailed investigation of the cation radicals of various aryl cyclopropanes generated by CAN has been reported recently.[251] A facile CAN-mediated oxidative rearrangement of alkoxyaryl cyclobutanes has been reported from our laboratory.[183] It was found that treatment of the cyclobutane **450** with CAN in dry methanol in an oxygen atmosphere led to formation of the keto methoxy product **451**. Illustrative examples of paracyclophane cleavage and cyclobutane cleavage are provided in Scheme 62.

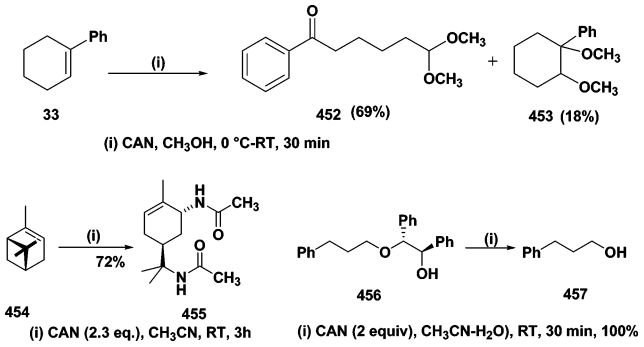
Nair and co-workers showed that CAN-mediated fragmentation of phenyl cycloalkenes led to the direct synthesis of monoacetals of 1,*n*-dicarbonyl compounds in good yields.[252] The radical cation generated from monoterpenes such as (+)-α-pinene **454** with CAN reacted in acetonitrile to afford the bisamide **455** in good yields.[253] Recent studies have also shown that CAN is a good reagent for removal of the hydroxyethyl unit from 2-hydroxyethyl ether derivatives **456** leading to alcohols.[254] Illustrative examples of these three processes are depicted in Scheme 63.

Fragmentation of azines to aldehydes and ketones was achieved using CAN in aqueous acetonitrile. Aldazines were

Scheme 62

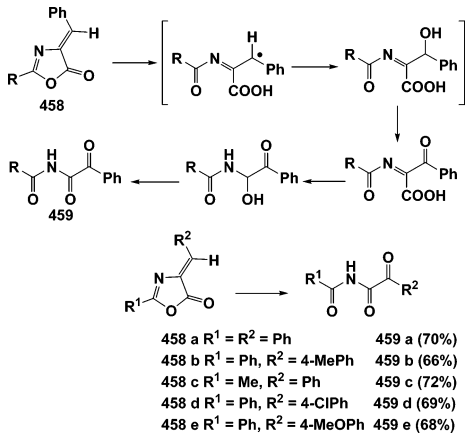


Scheme 63



converted to aldehydes without further oxidation.[255] CAN-promoted oxidative cleavage of azlactones resulted in the synthesis of α-oxocarboxamides. The iminodihydro cinnamic acid intermediate initially formed gets converted to the product through decarboxylation and subsequent oxidation (Scheme 64).[256]

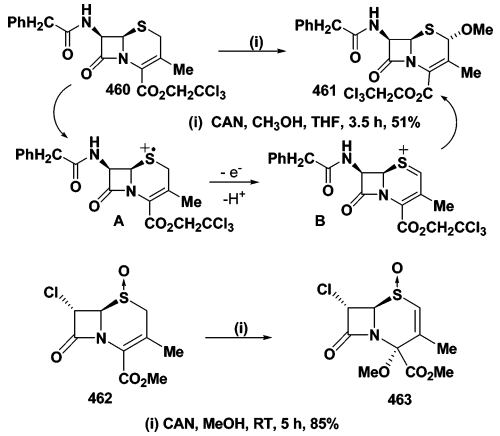
Scheme 64



6.2. Alkoxylation Reactions

Cephalosporins have been reported to react with CAN in methanol under mild conditions to give its corresponding 2-methoxy derivative as a major product along with very small amounts of thiazole derivatives.[257] Mechanistically, a single-electron transfer from sulfur to Ce(IV) reagent initiates the reaction forming **A**. The latter subsequently loses a proton and an electron to form **B** (Scheme 65). Cepham sulfoxides and sulfones, lacking an easily oxidizable sulfur atom, get alkoxylated stereoselectively at the C-4 position.[258] Formation of the compound can be rationalized as the result of a rare oxidative allylic rearrangement of cephalosporins wherein the alkoxy group is delivered with high face selectivity.

Scheme 65



In addition to the above, several other alkoxylation reactions have also been devised. Kim and co-workers reported a highly regioselective and stereoselective oxidative cyclization of cyclooctenols mediated by CAN.[259] Oxidative cyclization of compounds containing a double bond in the β position to a TMS group led to the corresponding tetrahydrofuran, tetrahydropyran, and piperidine analogs depending on whether the nucleophile is a hydroxy or an amide group.[260] Generation of cation radical from styrene moiety followed by ring closure with carboxy group is well known in CAN chemistry. This strategy has been used by Chavan and co-workers for conversion of β,γ-unsaturated acids into butenolides mediated by CAN. They applied this protocol for the synthesis of biologically active molecules such as heritonin.[261]

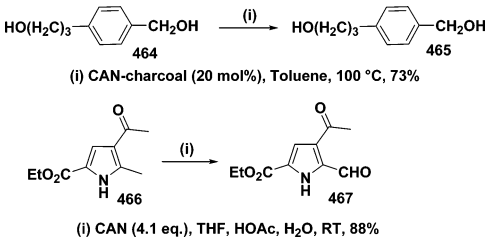
6.3. Side-Chain Oxidations

CAN has proved to be very useful for benzylic oxidations. Benzylic methyls are converted to aldehydes, while benzylic methylenes are converted to ketones by CAN in high yield. Trahanovsky demonstrated that toluenes can be oxidized to the corresponding benzaldehydes on treatment with CAN in 50% aq acetic acid, whereas in anhydrous acetic acid CAN oxidizes toluenes to benzyl acetates.[35] When multiple oxidation sites are available, the reaction normally stops at the monocarbonyl stage as in the oxidation of mesitylene to 3,5-dimethyl benzaldehyde in 100% yield. Methoxylation of 4-methyl anisole by reaction of CAN with methanol as the solvent has been reported.[262] A convenient procedure for the side-chain oxidation of pyrrole α-methyl to formyl was developed by Lightner.[263] It was found that the reaction largely depends on the choice of the solvent, reaction conditions, and the presence of a carboxylic ester group at the pyrrole α′ position. The latter uniquely activates the α-methyl group and causes the reaction to proceed more smoothly. Cerium(IV) ammonium nitrate adsorbed on activated charcoal has been found to be an effective catalyst for oxidation of benzyl alcohols and acyloins to the corresponding carbonyl compounds.[264] Scheme 66 provides some examples of typical side-chain oxidations by CAN. It was also observed that 1,2-benzoquinone formed by treatment of the parent catechol with CAN in methanol at −78 °C underwent facile [4+2] cycloaddition with indole to afford cycloadduct.[265]

6.4. Esterification and Transesterification

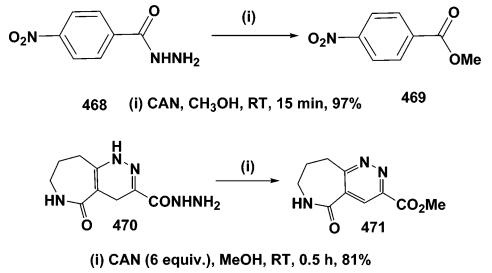
As early as 1972 Ho et al. showed that hydazides can be converted to acids by CAN.[266] Years later, work by another

Scheme 66



group showed that treatment of hydrazides with CAN in the presence of the appropriate alcohol as a nucleophile afforded esters in good yields.[267] The transformation involves selective oxidation of the hydrazino group in **468** followed by reaction with alcohols to yield ester **469**. The same group showed that pyridazino[4,3-*c*]azepine **470** gets converted to the corresponding ester **471** in moderate to high yields (Scheme 67). Thus, oxidation of the carbohydrazido group and

Scheme 67



aromatization of the 1,4-dihydropyridazine ring was achieved simultaneously.[268] CAN also acts as a mediator for transesterification reactions and esterification of carboxylic acids. The reaction probably occurs by the initial coordination of the carboxylic oxygen by Ce(IV) followed by nucleophilic attack by alcohol, leading to carboxylic esters. However, the transesterification method using CAN cannot be applied to substrates containing thiol or sulfide groups or 1,3-diketoesters due to their propensity to undergo oxidation.[269] Phenyl acetic acid and *cis*-oleic acid were esterified using CAN in the presence of primary and secondary alcohols, which also acted as the solvent.[270]

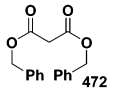
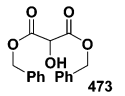
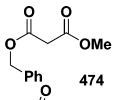
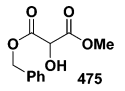
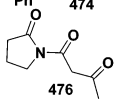
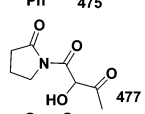
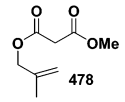
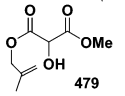
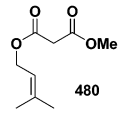
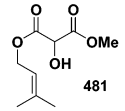
6.5. Dehydrogenation Reactions

CAN has also been used to promote certain dehydrogenation reactions. For instance, 1,4-dihydro-pyridine-3,5-dicarboxylates can be converted to the corresponding pyridine derivatives using CAN.[271] Dihydrotriazines obtained by reaction of monocyclic triazines with silyl enol ethers in the presence of ethyl chloroformates were oxidized by CAN in acetonitrile−water to afford 5-substituted 1,2,3-triazines.[272]

6.6. Other Synthetic Transformations

Treatment of dialkyl malonates with CAN in methanol by our group led to the direct synthesis of tartronic acid derivatives.[273] The reaction occurs by initial oxidation of malonate followed by its trapping with oxygen to form a peroxy radical and further transformations to form the product. Table 13 highlights some of the examples. The α-hydroxylation reaction of *β*-dicarbonyl compounds with molecular oxygen under Ce(IV) catalysis was studied extensively by Christoffers.[274] The role of the dioxygen is to oxidize the Ce(III) species to Ce(IV). The hydroxy group

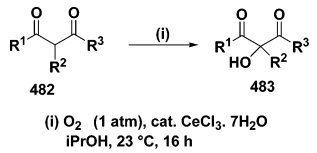
Table 13. Hydroxylation of *β*-Ketoesters with CAN[a]

Entry	Ester	Time (h)	Product	Yield (%)
1	 472	4	 473	60
2	 474	6	 475	62
3	 476	0.5	 477	69
4	 478	3	 479	23
5	 480	3	 481	25

[a] Reacton conditions: 2.3 equiv of CAN, MeOH, 0 °C to rt.

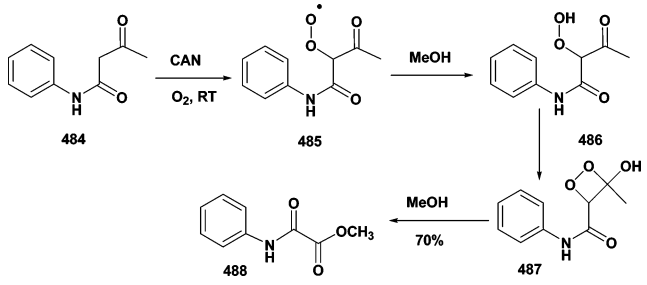
in the product **483** results from a nucleophilic attack of water on the electrophilic reaction intermediate (Scheme 68).

Scheme 68



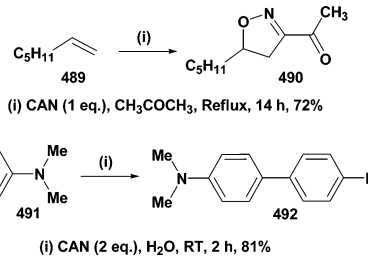
Reaction of acetoacetanilide **484** with CAN in methanol, carried out with the objective of executing an intramolecular reaction to derive the oxindole, afforded the corresponding oxamate in good yields. Substantial enhancement of the overall yield was attained when the reaction was performed in an atmosphere of oxygen.[275] The reaction can be rationalized as occurring via a dioxetane intermediate **487**. The latter is formed via the hydroperoxide **486**, which in turn is formed by reaction of atmospheric oxygen with the malonyl radical. The final step is fragmentation of dioxetanes in methanol and further transformations to afford the oxamate **488** (Scheme 69).

Scheme 69



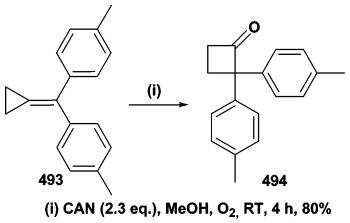
In addition, some other interesting transformations were also reported very recently. A mild method for oxidation of pyrazolines to pyrazoles was reported using CAN under MW irradiation.[276] Reaction of alkenes and alkynes with CAN under reflux conditions in acetone lead to formation of 3-acetyl-4,5-dihydroisoxazoles and 3-acetylisoxazole derivatives, respectively (Scheme 70).[277] Recently, oxidative coupling of *N*,*N*-dialkyl aryl amines **491** in water was

Scheme 70



reported to take place in the presence of CAN.[278] Recent work in our group has shown that CAN-mediated oxidation of methylenecyclopropane **493** led to a convenient synthesis of 2,2-diaryl cyclobutanone **494** by an oxidative ring-expansion reaction (Scheme 71).[279] Simultaneously, work by

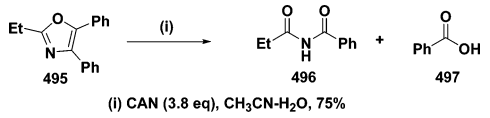
Scheme 71



Chen et al. on the CAN-mediated reaction of methylenecyclopropanes led to the synthesis of dihydrofurans and cyclobutanones.[280]

Very recent studies have shown that 4,5-diphenyl oxazoles can be oxidized to the corresponding imides in good yields by CAN (Scheme 72).[281] This reaction will allow use of the

Scheme 72



robust oxazole ring system as a surrogate amide in organic synthesis.

6.7. Polymerization Reactions

In addition to all the above reactions, CAN has been used as an initiator for a number of polymerization reactions, particularly for copolymerizations. Modification of biopolymers such as starch, cellulose, guargum, etc., was done using CAN as the initiator.[282,283] Mechanistically, the reaction takes place by the initial formation of a coordination complex between CAN and the biopolymer followed by disproportionation of the complex forming a free radical on the biopolymer chain and Ce(III). A detailed account of such reactions is beyond the scope of this review. Some of the current results are cited.[284−288]

7. Conclusions

It is evident from the above discussion that CAN acts as an efficient reagent for single-electron oxidation, and we hope that this review will encourage its use even more. Although there were many attempts to use CAN as a catalyst for several organic transformations, still there appears to be many potential possibilities for exploring the use of CAN as a catalyst. Another area in CAN chemistry which needs attention is use of CAN in asymmetric synthesis. It is reasonable to assume that work on these aspects of CAN chemistry will be very rewarding.

8. Acknowledgments

We thank Dr. Roshini Rajan for her help in the early stages of the preparation of this review. We thank all our former and present colleagues whose hard work has led to the emergence of CAN as a versatile and widely used reagent in organic synthesis. We also thank the Council of Scientific and Industrial Research for providing the financial assistance during production of this review.

9. References

(1) Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757.
(2) Gomberg, M. *Chem. Ber.* **1900**, *33*, 3150.
(3) Hey, D. H.; Waters, W. A. *Chem. Rev.* **1937**, *21*, 169.
(4) Kharasch, M. S. *J. Org. Chem.* **1937**, *2*, 400.
(5) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321.
(6) Stork, G. *Selectivity-A Goal for Synthetic Efficiency*; Verlag Chemie: Weinheim, 1981.
(7) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765.
(8) Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386.
(9) Julia, M. *Pure Appl. Chem.* **1974**, *40*, 553.
(10) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.
(11) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.
(12) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553.
(13) Curran, D. P. *Synthesis* **1988**, 489.
(14) Curran, D. P. *Synthesis* **1988**, 417.
(15) Pattenden, G.; Roberts, L.; Blake, A. J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 863.
(16) (a) Tsang, R.; Dickson, J. K.; Pak, H.; Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1987**, *109*, 3484. (b) Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1991**, *113*, 5791. (c) Henry, K. J., Jr.; Fraser-Reid, B. *J. Org. Chem.* **1994**, *59*, 5128.
(17) (a) Hart, D. J. *Science* **1984**, *223*, 883. (b) Hart, D. J.; Yang, T.-K. *J. Org. Chem.* **1985**, *50*, 235.
(18) Barton, D. H. R. *Aldrichim. Acta* **1990**, *23*, 3.
(19) Beckwith, A. L. J. *Chem. Soc. Rev.* **1993**, 143.
(20) Curran, D. P.; Jasperse, C. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237.
(21) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986.
(22) Becking, L.; Schafer, H. J. *Tetrahedron Lett.* **1988**, *29*, 2801.
(23) Cowan, D. O.; Drisko, R. L. *Elements of Photochemistry*; Plenum Press: New York, 1976.
(24) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339.
(25) Ho, T. L. *Synthesis* **1973**, 347.
(26) Ho, T. L. *Organic synthesis by oxidation with metal compounds*; Plenum Press: New York, 1986.
(27) Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573.
(28) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29.
(29) Imamoto, T. *Lanthanide reagents in organic synthesis*; Academic Press: London, 1994.
(30) Nair, V.; Mathew, J.; Radhakrishnan, K. V. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1487.
(31) Nair, V.; Mathew, J.; Prabhakaran, J. *Chem. Soc. Rev.* **1997**, 127.
(32) Hwu, J. R.; King, K. *Curr. Sci.* **2001**, *81*, 1043.
(33) Nair, V.; Panicker, S. B.; Nair, L. G.; George, T. G.; Augustine, A. *Synlett* **2003**, 156.
(34) Nair, V.; Balagopal, L.; Rajan, R.; Mathew, J. *Acc. Chem. Res.* **2004**, *37*, 21.
(35) (a) Trahanovsky, W. S.; Young, L. B. *J. Chem. Soc.* **1965**, 5777. (b) Trahanovsky, W. S.; Young, L. B. *J. Org. Chem.* **1967**, *32*, 3865.
(36) Trahanovsky, W. S.; Young, L. B. *J. Org. Chem.* **1966**, *31*, 2033.
(37) Syper, L. *Tetrahedron Lett.* **1966**, *37*, 4493.
(38) Trahanovsky, W. S.; Young, M. G.; Nave, P. M. *Tetrahedron Lett.* **1969**, *30*, 2501.
(39) Trahanovsky, W. S.; Young, L. H.; Bierman, M. H. *J. Org. Chem.* **1969**, *34*, 869.
(40) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 524.
(41) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 2888.
(42) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 995.
(43) Hay, N.; Kochi, J. K. *J. Inorg. Nucl. Chem.* **1968**, *30*, 884,
(44) (a) Norman, R. O. C.; Thomas, C. S.; Ward, P. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2914. (b) Kreh, R. P.; Spotnitz, R. M.; Lundquist, J. T. *J. Org. Chem.* **1989**, *54*, 1526. (c) Imamoto, T.; Koide, Y.; Hiyama, S. *Chem. Lett.* **1990**, *19*, 1445.

(45) (a) Dehmlow, E. V.; Makrandi, J. K. *J. Chem. Res. (S)* **1986**, *32*. (b) Muathen, H. A. *Ind. J. Chem*. **1991**, *30B*, 522.
(46) Chen, C.; Mariano, P. S. *J. Org. Chem*. **2000**, *65*, 3252.
(47) (a) Zhang, Y.; Flowers, R. A., II *J. Org. Chem*. **2003**, *68*, 4560. (b) Zhang, Y.; Raines, A. J.; Flowers, R. A., II *Org. Lett*. **2003**, *5*, 2363.
(48) Baciocchi, E.; Civatarese, G.; Ruzziconi, R. *Tetrahedron Lett*. **1987**, *28*, 5357.
(49) Baciocchi, E.; Ruzziconi, R. *Synth. Commun.* **1988**, *18*, 1841.
(50) Citterio, A.; Sebastiano, R.; Marion, A. *J. Org. Chem.* **1991**, *56*, 5328.
(51) Citterio, A.; Sebastiano, R.; Carvayal, M. C. *J. Org. Chem*. **1991**, *56*, 5335.
(52) Nair, V.; Mathew, J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 187.
(53) Nair, V.; Mathew, J.; Alexander, S. *Synth. Commun.* **1995**, *25*, 3981.
(54) Nair, V.; Mathew, J.; Nair, L. G. *Synth. Commun.* **1996**, *26*, 4531.
(55) Nair, V.; Nair, L. G.; Balagopal, L.; Mathew, J. *Ind. J. Chem.* **2000**, *39B*, 352.
(56) (a) Roy, S. C.; Mandal, P. K. *Tetrahedron* **1996**, *52*, 2193. (b) Roy, S. C.; Mandal, P. K. *Tetrahedron* **1996**, *52*, 12495.
(57) Hong, B. C.; Sun, H.-I.; Shr, Y.-J.; Lin, K.-J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2939.
(58) Ruzziconi, R.; Couthon-Gourvés, H.; Gourvés, J.-P.; Corbel, B. *Synlett* **2001**, 703.
(59) Lee, Y. R.; Kang, K. Y.; Lee, G. J.; Lee, W. K. *Synthesis* **2003**, 1977.
(60) Solabannavar, S. B.; Helavi, V. B.; Desai, U. V.; Mane, R. B. *Tetrahedron Lett.* **2002**, *43*, 4535.
(61) Szumny, A.; Wawrzenczyk, C. *Synlett* **2006**, 1523.
(62) Nair, V.; Suja, T. D.; Mohanan, K. *Synthesis* **2006**, 2335.
(63) Baciocchi, E.; Aira, D. D.; Ruzziconi, R. *Tetrahedron Lett.* **1986**, *27*, 2763.
(64) Mijs, W. J.; Jonge, C. R. H. *Organic Synthesis by Oxidation with Metal Compounds*; Plenum Press: New York, 1986.
(65) (a) Nair, V.; Mathew, J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1881. (b) Nair, V.; Mathew, J.; Nair, L. G. *Synth. Commun.* **1997**, *27*, 3053.
(66) (a) Linker, T.; Sommermann, T.; Kahlenberg, F. *J. Am. Chem. Soc.* **1997**, *119*, 9377. (b) Linker, T. *J. Organomet. Chem*. **2002**, *661*, 159.
(67) Tsai, A.-I.; Wu, Y.-L.; Chuang, C.-P. *Tetrahedron* **2001**, *57*, 7829.
(68) Kobayashi, K.; Mori, M.; Umed, T.; Morikawa, O.; Konishi, H. *Chem. Lett.* **1996**, *25*, 451.
(69) Nair, V.; Treesa, P. M.; Maliakal, D.; Rath, N. P. *Tetrahedron* **2001**, *57*, 7705.
(70) Kobayashi, K.; Uneda, T.; Mori, M.; Tanaka, K.; Tanaka, H.; Morikawa, O.; Konishi, H. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 1691.
(71) Kobayashi, K.; Sakashita, K.; Akamatsu, H.; Tanaka, K.; Uchida, M.; Uneda, T.; Kitamura, T.; Morikawa, O.; Konishi, H. *Heterocycles* **1999**, *51*, 2881.
(72) Kobayashi, K.; Tanaka, H.; Tanaka, K.; Yoneda, K.; Morikawa, O.; Konishi, H. *Synth. Commun*. **2000**, *30*, 4277.
(73) Kobayashi, K.; Umakoshi, H.; Hayashi, K.; Morikawa, O.; Konishi, H. *Chem. Lett*. **2004**, *33*, 1588.
(74) Skarżewski, J.; Zoń, J. *Synth. Commun.* **1995**, *25*, 2953.
(75) Ye, J.-H.; Xue, J.; Ling, K.-Q.; Xu, J.-H. *Tetrahedron Lett.* **1999**, *40*, 1365.
(76) Nicolaou, K. C.; Gray, D. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 761.
(77) (a) Baciocchi, E.; Casu, A.; Ruzziconi, R. *Tetrahedron Lett.* **1989**, *30*, 3707. (b) Baciocchi, E.; Casu, A.; Ruzziconi, R. *Synlett* **1990**, 679.
(78) Narasaka, K.; Okauchi, T. *Chem. Lett.* **1991**, *20*, 515.
(79) Narasaka, K.; Okauchi, T.; Tanaka, K.; Murakami, M. *Chem. Lett.* **1992**, *21*, 2099.
(80) Paolobelli, A. B.; Latini, D.; Ruzziconi, R. *Tetrahedron Lett*. **1993**, *34*, 721.
(81) Paolobelli, A. B.; Ceccherelli, P.; Pizzo, F.; Ruzziconi, R. *J. Org. Chem.* **1995**, *60*, 4954.
(82) Arai, N.; Narasaka, K. *Chem. Lett*. **1995**, *24*, 987.
(83) Paolobelli, A. B.; Ruzziconi, R. *J. Org. Chem.* **1996**, *61*, 6434.
(84) Lupattelli, P.; Ruzziconi, R.; Scafato, P. *J. Org. Chem.* **1998**, *63*, 4506.
(85) (a) Narasaka, K.; Kohno, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3456. (b) Narasaka, K.; Arai, N.; Okauchi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2995.
(86) Hwu, J. R.; Chen, C. N.; Shiao, S.-S. *J. Org. Chem.* **1995**, *60*, 856.
(87) (a) Baciocchi, E.; Giaccio, T. D.; Murgia, S. M.; Sebastiani, G. V. *Tetrahedron* **1988**, *44*, 6651. (b) Baciocchi, E.; Rol, C.; Sebastiani, G. V.; Zampini, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1045.
(88) (a) Nair, V.; Mathew, J.; Kanakamma, P. P.; Panicker, S. B.; Sheeba, V.; Zeena, S.; Eigendorf, G. K. *Tetrahedron Lett.* **1997**, *38*, 2191. (b) Nair, V.; Sheeba, V.; Panicker, S. B.; George, T. G.; Rajan, R.; Balagopal, L.; Vairamoni, M.; Prabhakar, S. *Tetrahedron* **2000**, *56*, 2461.
(89) Nair, V.; Nair, L. G.; Panicker, S. B.; Sheeba, V.; Augustine, A. *Chem. Lett.* **2000**, *29*, 584.
(90) Nair, V.; Rajan, R.; Rath, N. P. *Org. Lett.* **2002**, *4*, 1575.
(91) Kurz, M. E.; Ngoviwatchai, P. *J. Org. Chem.* **1981**, *46*, 4672.
(92) Kurz, M. E.; Baru, V.; Nguyen, P.-N. *J. Org. Chem.* **1984**, *49*, 1603.
(93) Mori, A.; Isayama, Y.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 511.
(94) Nakamura, A.; Kuto, K.; Ikeda, Y.; Mori, A.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2803.
(95) Jiang, P.; Lu, S. *Synth. Commun.* **2001**, *31*, 131.
(96) Tsvelikhovsky, D.; Schumann, H.; Blum, J. *Synthesis* **2006**, 1819.
(97) Haller, R.; Kohlmorgen, R.; Hänsel, W. *Tetrahedron Lett.* **1973**, 1205.
(98) Nagarajan, A.; Porcheziyan, V.; Srinivasaramanujam; Balasubramanian, T. R. *Ind. J. Chem.* **1985**, *24B*, 1202.
(99) Snider, B. B.; Kwon, T. *J. Org. Chem.* **1990**, *55*, 4786.
(100) Citterio, A.; Pesce, L.; Sebastiano, R.; Santi, R. *Synthesis* **1990**, 142.
(101) Baciocchi, E.; Paolobelli, A. B.; Ruzziconi, R. *Tetrahedron* **1992**, *48*, 4617.
(102) Takemoto, Y.; Ohra, T.; Furuse, S.-I.; Koike, H.; Iwata, C. *J. Chem. Soc., Chem. Commun.* **1994**, 1529.
(103) Takemoto, Y.; Ohra, T.; Koike, H.; Furuse, S.-I.; Iwata, C. *J. Org. Chem.* **1994**, *59*, 4727.
(104) Takemoto, Y.; Ibuka, T. Hayase, H.; Iwanaga, A.; Yamagata, S.; Iwata, C.; Tanaka, T. *Tetrahedron Lett.* **1998**, *39*, 7545.
(105) Takemoto, Y.; Furuse, S.-I.; Hayase, H.; Echigo, T.; Iwata, C.; Tanaka, T.; Ibuka, T. *J. Chem. Soc., Chem. Commun.* **1999**, 2515.
(106) Takemoto, Y.; Furuse, S.-I.; Koike, H.; Ohra, T.; Iwata, C.; Ohishi, H. *Tetrahedron Lett.* **1995**, *36*, 4085.
(107) Takemoto, T.; Yamagata, S.; Furuse, S.-I.; Hayase, H.; Echigo, T.; Iwata, C. *Chem. Commun.* **1998**, 651.
(108) D'Annibale, A.; Pesce, A.; Resta, S.; Trogolo, C. *Tetrahedron Lett.* **1997**, *38*, 1829.
(109) Iwaya, K.; Tamura, M.; Nakamura, M.; Hasegawa, E. *Tetrahedron Lett.* **2003**, *44*, 9317.
(110) Jamie, J. F.; Rickards, R. W. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2603.
(111) Kim, H. J.; Yoon, U. C.; Jung, Y.-S.; Park, N. S.; Cederstrom, E. M.; Mariano, P. S. *J. Org. Chem.* **1998**, *63*, 860.
(112) Durand, A.-C.; Dumez, E.; Rodriguez, J.; Dulcère, J.-P. *Chem. Commun.* **1999**, 2437.
(113) Durand, A.-C.; Rodriguez, J.; Dulcère, J.-P. *Synlett* **2000**, 731.
(114) Snider, B. B.; Shi, B.; Quickley, C. A. *Tetrahedron* **2000**, *56*, 10127.
(115) Langer, P.; Köhler, V. *Chem. Commun.* **2000**, 1653.
(116) Nair, V.; Balagopal, L.; Sheeba, V.; Panicker, S. B.; Rath, N. P. *Chem. Commun.* **2001**, 1682.
(117) Seiders, J. R.; Wang, L.; Floreancig, P. E. *J. Am. Chem. Soc*. **2003**, *125*, 2406.
(118) Wang, L.; Seiders, J. R., II; Floreancig, P. E. *J. Am. Chem. Soc*. **2004**, *126*, 12590.
(119) Clark, A. J.; Dell, C. P.; McDonagh, J. M.; Geden, J.; Mawdsley, P. *Org. Lett*. **2003**, *5*, 2063.
(120) Nair, V.; Balagopal, L.; Rajan, R.; Deepthi, A.; Mohanan, K.; Rath, N. P. *Tetrahedron Lett.* **2004**, *45*, 2413.
(121) Nair, V.; Mohanan, K.; Suja, T. D.; Suresh, E. *Tetrahedron Lett.* **2006**, *47*, 705.
(122) Nair, V.; Mohanan, K.; Suja, T. D.; Suresh, E. *Tetrahedron Lett*. **2006**, *47*, 2803.
(123) (a) Brimble, M. A.; Burgess, C.; Halim, R.; Petersson, M.; Ray, J. *Tetrahedron* **2004**, *60*, 5751. (b) Brimble, M. A.; Laita, O.; Robinson, J. E. *Tetrahedron* **2006**, *62*, 3021.
(124) Trahanovsky, W. S.; Robbins, M. D. *J. Am. Chem. Soc.* **1971**, *93*, 5256.
(125) Lemieux, R. U.; Ratcliffe, R. M. *Can. J. Chem.* **1979**, *57*, 1244.
(126) Clive, D. L. J.; Etkin, N. *Tetrahedron Lett.* **1994**, *35*, 2459.
(127) Nair, V.; George, T. G. *Tetrahedron Lett.* **2000**, *41*, 3199.
(128) Auberson, Y.; Vogel, P. *Tetrahedron* **1990**, *45*, 7019.
(129) Magnus, P.; Barth, L. *Tetrahedron Lett.* **1992**, *33*, 2777.
(130) Nair, V.; Nair, L. G.; George, T. G.; Augustine, A. *Tetrahedron* **2000**, *56*, 7607.
(131) Briguet, C.; Freppel, C.; Richer, J.-C.; Zador, M. *Can. J. Chem.* **1974**, *52*, 3201.
(132) Hwu, J. R.; Chen, K. L.; Ananthan, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1425.
(133) Hwu, J. R.; Chen, K. L.; Ananthan, S.; Patel, H. V. *Organometallics* **1996**, *15*, 499.
(134) Reddy, M. V. R.; Mehrotra, B.; Vankar, Y. D. *Tetrahedron Lett.* **1995**, *36*, 4861.
(135) Smith, C. C.; Jacyno, J. M.; Zeiter, K. K.; Parkansky, P. D.; Paxson, C. E.; Pekelnicky, P.; Harwood, J. S.; Hunter, A. D.; Lucarelli, V. G.; Lufas, M. W.; Cutler, H. G. *Tetrahedron Lett.* **1998**, *39*, 6617.
(136) Sakaguchi, S.; Hirabayashi, T.; Ishii, Y. *Chem. Commun*. **2002**, 516.
(137) Nair, V.; Suja, T. D.; Mohanan, K. *Tetrahedron Lett*. **2005**, *46*, 3217.
(138) Bandgar, B. P.; Makone, S. S. *Synlett* **2003**, 262.

(139) Rao, A. S.; Srinivas, P. V.; Babu, S.; Rao, J. M. *Tetrahedron Lett.* **2005**, *46*, 8141.
(140) Varala, R.; Enugala, R.; Nuvula, S.; Adapa, S. R. *Synlett* **2006**, 1009.
(141) Varala, R.; Nuvula, S.; Adapa, S. R. *Synlett* **2006**, 1549.
(142) Chawla, H. M.; Mittal, R. S. *Synthesis* **1985**, 70.
(143) Mellor, J. M.; Parkes, R.; Millar, R. W. *Tetrahedron Lett.* **1997**, *38*, 8739.
(144) Chawla, H. M.; Mittal, R. S. *Ind. J. Chem.* **1983**, *1983*, 751.
(145) Grenier, J.-L.; Catteau, J.-P.; Cotelle, P. *Synth. Commun.* **1999**, *29*, 1201.
(146) Mellor, J. M.; Mittoo, S.; Parkes, R.; Millar, R. W. *Tetrahedron* **2000**, *56*, 8019.
(147) Ganguly, N.; Sukai, A. K.; De, S. *Synth. Commun*. **2001**, *31*, 301.
(148) Yang, X.; Xi, C.; Jiang, Y. *Tetrahedron Lett.* **2005**, *46*, 8781.
(149) Narasaka, K.; Mochizuki, T.; Hayakawa, S. *Chem. Lett.* **1994**, *23*, 1705.
(150) Mochizuki, T.; Hayakawa, S.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2317.
(151) Nair, V.; Augustine, A.; George, T. G.; Nair, L. G. *Tetrahedron Lett.* **2001**, *42*, 6763.
(152) Nair, V.; Nair, L. G. *Tetrahedron Lett.* **1998**, *39*, 4585.
(153) Nair, V.; George, T. G.; Nair, L. G.; Panicker, S. B. *Tetrahedron Lett.* **1999**, *40*, 1195.
(154) Nair, V.; George, T. G.; Augustine, A.; Nair, L. G. *Res. Chem. Intermed.* **2000**, *26*, 923.
(155) Bosman, C.; Annibale, A. D.; Resta, S.; Trogolo, C. *Tetrahedron Lett.* **1994**, *35*, 6525.
(156) Nair, V.; Augustine, A.; George, T. G. *Eur. J. Org. Chem.* **2002**, 2363.
(157) Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2847.
(158) Horiuchi, C. A.; Takahashi, E. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 271.
(159) Horiuchi, C. A.; Kiji, S. *Chem. Lett.* **1988**, *17*, 31.
(160) Horiuchi, C. A.; Ochiai, K.; Fukunishi, H. *Chem. Lett.* **1994**, *23*, 185.
(161) Horiuchi, C. A.; Fukunishi, H.; Kajita, M.; Yamaguchi, A.; Kiyomiya, H.; Kiji, S. *Chem. Lett*. **1991**, *20*, 1921.
(162) Horiuchi, C. A.; Nishio, Y.; Gong, D.; Fujisaki, T.; Kiji, S. *Chem. Lett.* **1991**, *20*, 607.
(163) Horiuchi, C. A.; Hosokawa, H.; Kanamori, M.; Muramatsu, Y.; Ochiai, K.; Takahashi, E. *Chem. Lett.* **1995**, *24*, 13.
(164) Horiuchi, C. A.; Ikeda, A.; Kanamori, M.; Hosokawa, H.; Sugiyama, T.; Takahashi, T. *J. Chem. Res. (S)* **1997**, *60*.
(165) Zhang, F. J.; Li, Y. L. *Synthesis* **1993**, 565.
(166) Asakura, J.; Robins, M. J. *Tetrahedron Lett.* **1988**, *29*, 2859.
(167) Roush, W. R.; Narayan, S.; Bennett, C. E.; Briner, K. *Org. Lett.* **1999**, *1*, 895.
(168) Rodríguez-Franco, M. I.; Dorronsoro, I.; Hernández-Higueras, A. I.; Antequera, G. *Tetrahedron Lett.* **2001**, *42*, 863.
(169) Baciocchi, E.; Crescenzi, M. *Tetrahedron* **1988**, *44*, 6525.
(170) Asakura, J.; Robins, M. J. *J. Org. Chem.* **1990**, *55*, 4928.
(171) Nair, V.; Panicker, S. B.; Augustine, A.; George, T. G.; Thomas, S.; Vairamani, M. *Tetrahedron* **2001**, *57*, 7417.
(172) Roy, S. C.; Guin, C.; Rana, K. K.; Maiti, G. *Synlett* **2001**, 226.
(173) Nair, V.; George, T. G.; Sheeba, V.; Augustine, A.; Balagopal, L.; Nair, L. G. *Synlett* **2000**, 1597.
(174) Iranpoor, N.; Baltork, I. M.; Zardaloo, F. S. *Tetrahedron* **1991**, *47*, 9861.
(175) Roy, S. C.; Adhikari, S. *Ind. J. Chem.* **1992**, *31B*, 459.
(176) Iranpoor, N.; Kazemi, F.; Salehi, P. *Synth. Commun.* **1997**, *27*, 1247.
(177) Iranpoor, N.; Salehi, P. *Tetrahedron* **1995**, *51*, 909.
(178) Fabio, R. D.; Rossi, T.; Thomas, R. J. *Tetrahedron Lett.* **1997**, *38*, 3587.
(179) Hanson, J. R.; Troussier, M.; Uyanik, C.; Viel, F. *J. Chem. Res. (S*) **1998**, 118.
(180) Iranpoor, N.; Kazemi, F. *Synth. Commun.* **1999**, *29*, 561.
(181) Iranpoor, N.; Kazemi, F. *Synthesis* **1996**, 821.
(182) Chandrashekar, S.; Narsihmulu, C.; Sultana, S. S. *Tetrahedron Lett.* **2002**, *43*, 7361.
(183) Nair, V.; Rajan, R.; Mohanan, K.; Sheeba, V. *Tetrahedron Lett.* **2003**, *44*, 4585.
(184) Chakraborty, T. K.; Ghosh, A.; Raju, T. V. *Chem. Lett*. **2003**, *32*, 82.
(185) Surendra, K.; Krishnaveni, S.; Rao, K. R. *Tetrahedron Lett.* **2005**, *46*, 4111.
(186) Ho, T. L. *Synthesis* **1978**, 936.
(187) Ganin, B.; Amer, I. *Synth. Commun.* **1995**, *25*, 3149.
(188) Olah, G. A.; Gupta, B. G. B.; Fung, A. P. *Synthesis* **1980**, 897.
(189) Tomioka, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 539.
(190) Goswami, P.; Chowdhury, P. *New J. Chem.* **2000**, *24*, 955.
(191) Tanemura, K.; Suzuki, T.; Nishida, Y.; Satsumabayashi, K.; Horaguchi, T. *Chem. Lett.* **2001**, *30*, 1012.
(192) Takarada, T.; Yashiro, M.; Komiyamo, M. *Chem. Eur. J.* **2000**, *6*, 3906.
(193) Ramesh, C.; Ravindranath, N.; Das, B. *J. Chem. Res. (S*) **2003**, 72.
(194) Ji, S.; Wang, S. *Synlett* **2003**, 2074.
(195) Ko, S.; Lin, C.; Tu, Z.; Wang, Y.-F.; Wang, C.-C.; Yao, C.-F. *Tetrahedron Lett.* **2006**, *47*, 487.
(196) Wang, S.-Y.; Ji, S.-J. *Tetrahedron* **2006**, *62*, 1527.
(197) Han, B.; Jia, X.-D.; Jin, X.-L.; Zhou, Y.-L.; Yang, L.; Liu, Z.-L.; Yu, W. *Tetrahedron Lett.* **2006**, *47*, 3545.
(198) Savitha, G.; Perumal, P. T. *Tetrahedron Lett.* **2006**, *47*, 3589.
(199) Watts, L.; Fitzpatrick, J. D.; Petit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253.
(200) Reeves, P.; Henery, J.; Pettit, R. *J. Am. Chem. Soc.* **1969**, *91*, 5888.
(201) Holmes, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *85*, 2531.
(202) Gibson, D. H.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 2620.
(203) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1975**, *102*, 175.
(204) Wulff, W. D.; Tang, P. C.; McCallum, J. S. *J. Am. Chem. Soc*. **1981**, *103*, 7677.
(205) Bird, J. W.; Diaper, D. G. M. *Can. J. Chem.* **1969**, *47*, 145.
(206) Ho, T.-L. *J. Chem. Soc., Chem. Commun.* **1972**, 791.
(207) Ho, T.-L.; Hall, J.-W.; Wong, C. M. *Chem. Ind. (London*) **1972**, 729.
(208) Tanoue, Y.; Terada, A. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2039.
(209) Bauer, H.; Briane, J.; Staab, H. A. *Angew. Chem., Int. Ed. Engl*. **1983**, *22*, 334.
(210) Corey, E. J.; Tramontano, A. *J. Am. Chem. Soc*. **1981**, *103*, 5599.
(211) Halton, B.; Kay, A. J.; Zhi-mei, Z.; Boese, R.; Haumann, T. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1445.
(212) Valderrama, J. A.; Valderrama, C. *Synth. Commun*. **1997**, *27*, 2143.
(213) Cotelle, P.; Catteau, J.-P. *Tetrahedron Lett.* **1992**, *33*, 3855.
(214) Nair, V.; Nair, L. G.; Balagopal, L.; Rajan, R. *Ind. J. Chem.* **1999**, *38B*, 1234.
(215) Ates, A.; Gautier, A.; Leroy, B.; Plancher, J.-M.; Quesnel, Y.; Markó, I. E. *Tetrahedron Lett.* **1999**, *40*, 1799.
(216) Markó, I. E.; Ates, A.; Gautier, A.; Leroy, B.; Plancher, J.-M.; Quensel, Y.; Vanherck, J.-C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3207.
(217) Maulide, N.; Markó, I. E. *Synlett* **2005**, 2195.
(218) Gupta, A. D.; Singh, R.; Singh, V. K. *Synlett* **1996**, 69.
(219) Marko, I. E.; Ates, A.; Augustyns, B.; Gautier, A.; Quesnel, Y.; Turet, L.; Wiaux, M. *Tetrahedron Lett.* **1999**, *40*, 5613.
(220) Palomo, C.; Aizpurua, J. M.; Legido, M.; Mielgo, A.; Galarza, R. *Chem. Eur. J*. **1997**, *3*, 1432.
(221) Hwu, J. R.; Jain, M. L.; Tsay, S.-C.; Hakemelahi, G. H. *Tetrahedron Lett.* **1996**, *37*, 2035.
(222) Hwu, J. R.; Jain, M. L.; Tsay, S.-C.; Hakimelahi, G. H. *Chem. Commun.* **1996**, 545.
(223) Hudlicky, M. *J. Org. Chem*. **1974**, *39*, 3460.
(224) Taylor, E. C.; Chiang, C. S.; McKillop, A.; White, J. F. *J. Am Chem. Soc*. **1976**, *98*, 6750.
(225) Keinan, E.; Mazur, Y. *J. Org. Chem*. **1978**, *43*, 1027.
(226) Diddams, P. In *Solid Supports and Catalysts in Organic Synthesis*; Smith, K., Ed.; Ellis Horwood: New York, 1992; Chapter 1.
(227) Hwu, J. R.; Jain, M. L.; Tsai, F.-Y.; Tsay, S.-C.; Balakumar, A.; Hakimelahi, G. H. *J. Org. Chem*. **2000**, *65*, 5077.
(228) Bull, S. D.; Davies, S. G.; Fenton, G.; Mulvaney, A. W.; Prasad, S. R.; Smith, A. D. *Chem. Commun.* **2000**, 337.
(229) Bull, S. D.; Davies, S. G.; Fenton, G.; Mulvaney, A. W.; Prasad, R. S.; Smith, A. D. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3765.
(230) Wright, J. A.; Yu, J.; Spencer, J. B. *Tetrahedron Lett.* **2001**, *42*, 4033.
(231) Podlech, J. *Synth. Commun*. **2000**, *30*, 1779.
(232) Podlech, J.; Steurer, S. *Synthesis* **1999**, 650.
(233) Hasegawa, M.; Taniyama, D.; Tomioka, K. *Tetrahedron* **2000**, *56*, 10153.
(234) Gordon, K. H.; Balasubramanian, S. *Org. Lett.* **2001**, *3*, 53.
(235) (a) Fetter, J.; Keskeny, E.; Czuppon, T.; Lempert, K.; Kajtár-Peredy, M.; Tamás, J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3061. (b) Giang, L. T.; Fetter, J.; Lempert, K.; Kajtár-Peredy, M.; Gömöry, Á. *Tetrahedron* **1996**, *52*, 10169.
(236) Iranpoor, N.; Mothaghineghad, W. *Tetrahedron* **1994**, *50*, 1859.
(237) Manzo, E.; Barone, G.; Parrilli, M. *Synlett* **2000**, 887.
(238) Pachamuthu, K.; Vankar, Y. D. *J. Org. Chem*. **2001**, *66*, 7511.
(239) Nair, V.; Rajan, R.; Balagopal, L.; Nair, L. G.; Ros, S.; Mohanan, K. *Ind. J. Chem.* **2005**, *44B*, 141.
(240) Comin, M. J.; Elhalem, E.; Rodriguez, J. B. *Tetrahedron* **2004**, *60*, 11851.
(241) Shindalkar, S. S.; Madje, B. R.; Hangarge, R. V.; Shingare, M. S. *Ind. J. Chem*. **2005**, *446*, 2409.
(242) Soucy, P.; Ho, T.-L.; Deslongchamps, P. *Can. J. Chem.* **1972**, *50*, 2047.
(243) Balasubramanian, V.; Robinson, C. H. *Tetrahedron Lett.* **1981**, *22*, 501.

(244) (a) Chang, M.-Y.; Lin, C.-Y.; Pai, C.-L. *Tetrahedron Lett*. **2006**, *47*, 2565. (b) Chang, M.-Y.; Wu, T.-C.; Lin, C.-Y.; Hung, C.-Y. *Tetrahedron Lett*. **2006**, *47*, 8347.
(245) Trahanovsky, W. S.; Himstedt, A. L. *J. Am. Chem. Soc*. **1974**, *96*, 1166.
(246) Wilson, S. R.; Zucker, R. A.; Kim, C.-W.; Villa, C. A. *Tetrahedron Lett*. **1985**, *26*, 1969.
(247) Hwu, J. R.; Shiao, S.-S.; Tsay, S.-C. *J. Am. Chem. Soc*. **2000**, *122*, 5899.
(248) Adam, W.; Miranda, M. A.; Mojarrad, F.; Sheikh, H. *Chem. Ber*. **1994**, *127*, 875.
(249) Young, L. B. *Tetrahedron Lett.* **1968**, *9*, 5105.
(250) Corey, E. J.; Arnold, Z.; Hutton, J. *Tetrahedron Lett.* **1970**, *11*, 307.
(251) Wang, Y.; Tanko, J. M. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2705.
(252) Nair, V.; Panicker, S. B. *Tetrahedron Lett.* **1999**, *40*, 563.
(253) Nair, V.; Rajan, R.; Balagopal, L.; Thomas, S.; Narasimlu, K. *Tetrahedron Lett.* **2002**, *43*, 8971.
(254) Fujioka, H.; Ohba, Y.; Hirose, H.; Mural, K.; Kita, Y. *Org. Lett*. **2005**, *7*, 3303.
(255) Giurg, M.; Mlochowski, J. *Synth. Commun*. **1999**, *29*, 4307.
(256) Ram, S. R.; Rama Devi, A.; Iyengar, D. S. *Chem. Lett*. **2002**, *31*, 718.
(257) Fletton, R. A.; Humber, D. C.; Roberts, S. M.; Wright, J. L. *J. Chem. Soc., Perkin Trans 1* **1985**, 1523.
(258) Alpegiani, M.; Bissolino, P.; Borghi, D.; Perrone, E. *Synlett* **1994**, 233.
(259) Kim, H.; Schlecht, M. F. *Tetrahedron Lett.* **1988**, *29*, 1771.
(260) Wilson, S. R.; Angelli-Szafran, C. E. *Tetrahedron* **1988**, *44*, 3983.
(261) Chavan, S. P.; Zubaidha, P. K.; Govande, C. A.; Subba Rao, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1101.
(262) Dallacort, A. D.; Barbera, A. L.; Mandolini, L. *J. Chem Res. (S*) **1983**, 44.
(263) Thyrann, T.; Lightner, D. A. *Tetrahedron Lett.* **1995**, *36*, 4345.
(264) Hatanaka, Y.; Imamoto, T.; Yokoyama, M. *Tetrahedron Lett.* **1983**, *24*, 2399.
(265) Omote, Y.; Tomotake, A. *J. Chem. Res. (S*) **1987**, 10.
(266) Ho, T.-L.; Ho, C. H.; Wong, C. M. *Synthesis* **1972**, 562.
(267) Štefani, B.; Kočevar, M.; Polanc, S. *Tetrahedron Lett.* **1999**, 40, 4429.
(268) Požgan, F.; Polanc, S.; Kočevar, M. *Synthesis* **2003**, 2349.
(269) Štefane, B.; Kočevar, M.; Polanc, S. *Synth. Commun.* **2002**, *32*, 1703.
(270) Pan, W.-B.; Chang, F.-R.; Wei, L.-M.; Wu, M.-J.; Wu, Y.-C. *Tetrahedron Lett.* **2003**, *44*, 331.
(271) Pfister, J. R. *Synthesis* **1990**, 689.
(272) Itoh, T.; Matsuya, Y.; Hasegawa, H.; Nagata, K.; Okada, M.; Ohsawa, A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2511.
(273) Nair, V.; Nair, L. G.; Mathew, J. *Tetrahedron Lett.* **1998**, *39*, 2801.
(274) (a) Christoffers, J.; Werner, T. *Synlett* **2002**, 119. (b) Christoffers, J.; Baro, A.; Werner, T. *Adv. Synth. Catal*. **2004**, *346*, 143. (c) Christoffers, J.; Kauf, T.; Werner, T.; Rössle, M. *Eur. J. Org. Chem*. **2006**, 2601.
(275) Nair, V.; Sheeba, V. *J. Org. Chem.* **1999**, *64*, 6898.
(276) Mogilaiah, K.; Reddy, N. V.; Rao, R. B. *Ind. J. Chem*. **2003**, *42B*, 2618.
(277) Itoh, K.; Horiuchi, C. A. *Tetrahedron* **2004**, *60*, 1671.
(278) Xi, C.; Jiang, Y.; Yang, X. *Tetrahedron Lett.* **2005**, *46*, 3909.
(279) Nair, V.; Suja, T. D.; Mohanan, K. *Synthesis* **2006**, 2531.
(280) Chen, W.; Huang, K.; Zhou, H.; Ren, L. *Synthesis* **2006**, 609.
(281) Evans, D. A.; Nagorny, P.; Xu, R. *Org. Lett*. **2006**, *8*, 5669.
(282) Athawale, V. D.; Lele, V. *Carbohydr. Polym*. **2000**, *41*, 407.
(283) Ren, L.; Tokura, S. *Carbohydr. Polym*. **1994**, *23*, 19.
(284) Sharma, B. R.; Kumar, V.; Soni, P. L. *J. Appl. Polym. Sci*. **2002**, *86*, 3250.
(285) Song, Y.; Jin, Y.; Wei, D.; Sun, J. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2006**, *43*, 899.
(286) Luckachen, G. E.; Jose, L.; Prasad, V. S.; Pillai, C. K. S. *Polym. Degrad. Stab.* **2006**, *91*, 1484.
(287) Joshi, J. M.; Sinha, V. *Polymer* **2006**, *47*, 2198.
(288) Song, Y.; Wei, D. *Polym. Polym. Compos.* **2006**, *14*, 169.

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