Versatile reagent ceric ammonium nitrate in modern chemical synthesis

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Most reagents play a single role in chemical reactions of various types. Ceric ammonium nitrate is an orange solid and commercially available. It has been widely used in industry and academia during the past six decades. In this review, the role, efficiency, and advantages of ceric ammonium nitrate are discussed for its use with versatile roles in different chemical transformations. These reactions include carbon–carbon bond formation, oxidative carbon–carbon bond cleavage, nitration, and removal of protecting groups. The information will be of value to chemical synthesis of new compounds and materials.

IN 1936, Smith et al.[1] invented a new chemical agent ceric ammonium nitrate (CAN), which is also named ammonium cerium(IV) nitrate, ammonium hexanitratocerate(IV), or ammonium nitratocerate(IV). It is prepared from fresh ceric hydrate or oxide in an excess amount of nitric acid and then with a quantitative amount of ammonium salt. Crystallized CAN in orange colour can be obtained by evaporation of the solvent at low temperatures. X-Ray crystallography of CAN shows that cerium(IV) locates at the center of the anion complexed by six bidentate nitrate groups[2]. Thus the formula can be written as $(NH_4)_2[Ce(NO_3)_6]$. Being a non-hygroscopic solid, this reagent is readily available in pure form and can be handled easily.

The solubility of CAN in water is 1.41 g/ml at 25°C and 2.27 g/ml at 80°C (ref. 3). It is to a smaller extent in polar organic solvents, such as acetic acid. In redox reactions, CAN functions as an oxidant. Its consumption can be judged by colour change from orange to pale yellow or colourless if the substrate and the product are not strongly coloured. Because of its extremely limited solubility in common organic solvents, reactions involving CAN are often carried out in mixed water–organic solvents, such as aqueous acetonitrile. Hitherto, the toxicity of CAN has not been elucidated.

In industry, solution of CAN in dilute perchloric acid is used as etchants for preparation of printed circuits, metal samples, and for surface cleaning prior to fabrication by soldering[4]. This blend is particularly useful in the etching of alloys, monel, nichrome, and stainless steel. In academia, CAN is explored extensively in organic reactions. Representative examples include oxidation[5–13], oxidative addition[14–21], photooxidation[22,23], nitration[24–28], deprotection[29–35], graft polymerization[36–41], etc. Intermediates formed in these reactions may undergo oxidative fragmentation[42,43], rearrangement[44–47], or cleavages of C–H and C–C bonds[48,49].

In the Third World, many research groups successfully developed useful transformations by application of this reagent. For example, Chavan and Subbarao[50] developed a CAN-mediated azidoalkoxylation of enol ethers and olefins (Scheme 1). Polanc et al.[51] established a selective conversion of hydrazides to esters by using CAN in the presence of alcohol (Scheme 2). Markó et al.[31] applied CAN as a catalyst in the deprotection of acetals to give the parent ketones (Scheme 3). Arslan and Hazer[41] reported a polymerization of methyl methacrylate initiated by CAN in combination with polytetrahydrofuran diol and polycaprolactone diol (see Scheme 4).

Recently, our research groups has been investigating on new chemical transformations with synthetic applicability by using CAN. In this review, we wish to report our design on these transformations, their significance, and advantages associated with the use of CAN.

Carbon–carbon single bond formation

Allylation of carbonyl compounds with allyltrimethylsilane

Many complex compounds with biological activities can be prepared from small molecules through carbon–carbon single bond formation. Introduction of an allyl group at an α position of carbonyl compounds often encounters a problem resulting from the competing oxygen–carbon bond formation. Moreover, anhydrous conditions are usually required for high yields of the desired products.

Use of CAN (2.1 equiv) in methanol allows the conversion of cycloalkanones with five- to eight- and twelve-membered ring to the corresponding monoallylated products in 21–75% yields at 25°C (Scheme 5, ref.
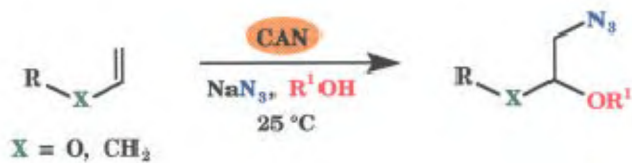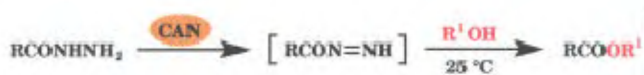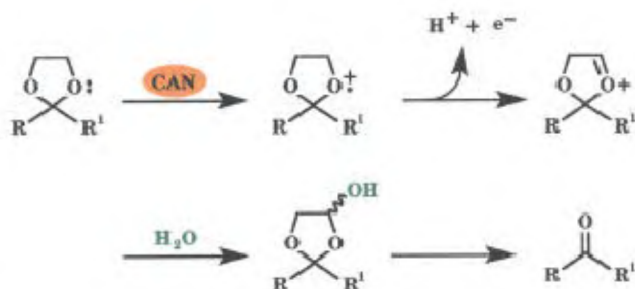
Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.
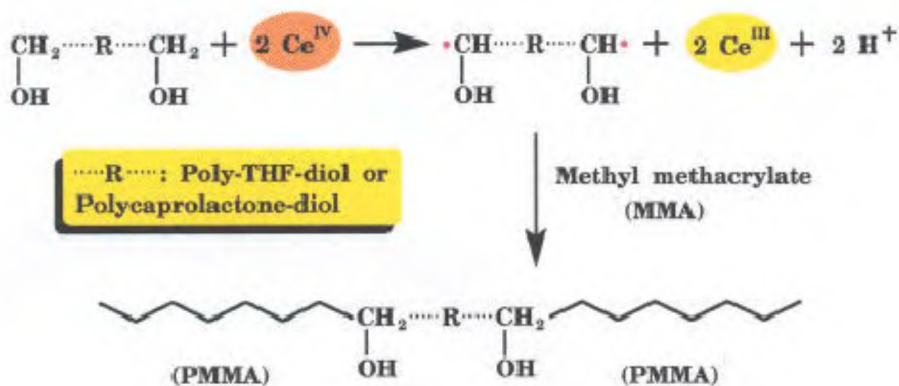
n =	% yield
1	35
2	39
3	21
4	25
8	75

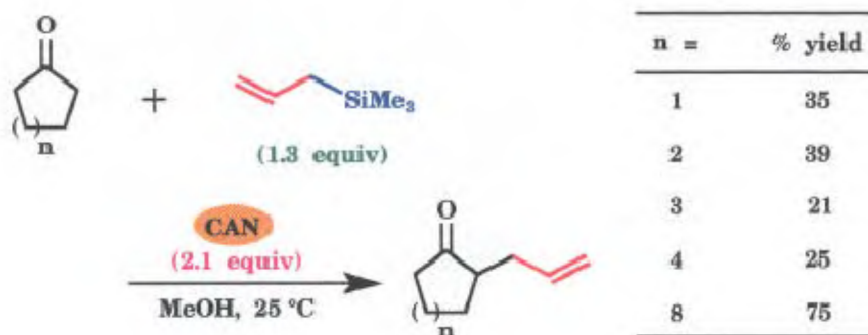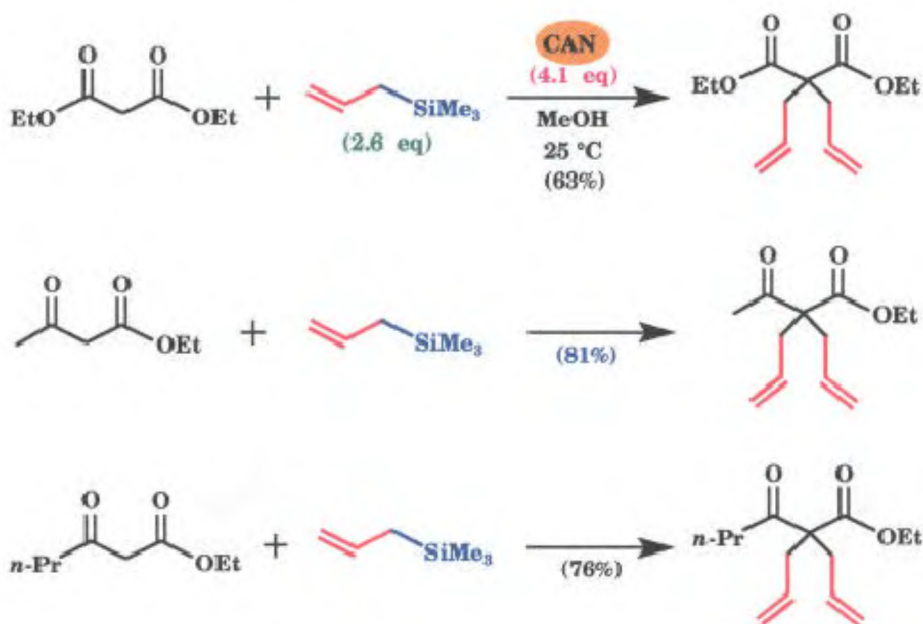**Scheme 5.**

20). 1,3-Diketones, such as 2,2,6,6-tetramethyl-3,5-heptanedione and diethyl malonate, can also be converted to the corresponding monoallylated products in 74–98% yields under the same conditions. In all of these reactions, the carbon–carbon bond formation takes place exclusively at the terminal sp^2 carbon of allyltrimethylsilane; no products are generated through the oxygen–carbon bond formation. Use of an excess of allyltrimethylsilane (e.g. 2.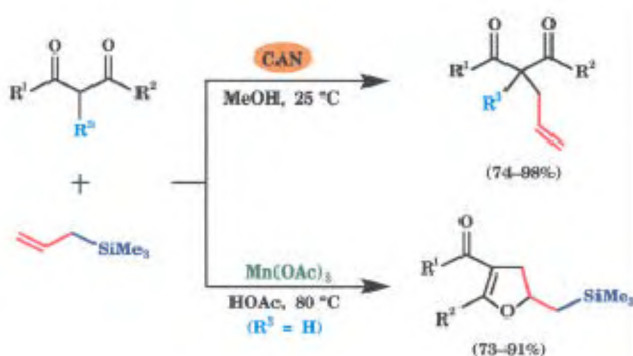6 equiv) to react with 1,3-dioxo compounds in the presence of CAN (4.1 equiv) affords diallylated products in 63–81% yields (see Scheme 6).

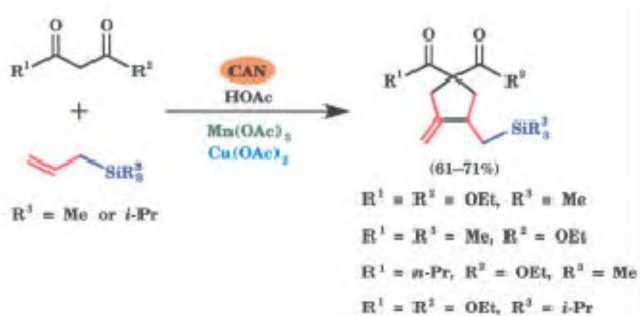*Allylation of 1,3-dioxo compounds vs formation of dihydrofurans*

Ceric ammonium nitrate[15] (CAN) and manganese(III)[52] acetate can initiate oxidative additions of 1,3-dioxo compounds to alkenes through one-electron transfer

Scheme 6.

Scheme 7.

Scheme 8.

process[53]. These reactions often produce nitrate esters or dihydrofurans or both[54,55]. Introduction of a trimethylsilyl group onto the alkenes allows these compounds to add oxidatively to 1,3-dioxo compounds through C-allylation (Scheme 7, ref. 21). Then elimination of the trimethylsilyl group takes place to afford the allylated 1,3-dioxo compounds in good to excellent yields. Use of $Mn(OAc)_3 \cdot 2H_2O$ and acetic acid to replace CAN and methanol for initiation of the reaction between allyltrimethylsilane and a 1,3-diketone or a β-keto ester produces silicon-containing dihydrofurans in 73–91% yields[21].

Often the addition of 1,3-dioxo compounds to alkenes in the presence of CAN or $Mn(OAc)_3 \cdot 2H_2O$ goes through carboradical intermediates[54,55]. The diversity of products likely comes from the reactivity difference between CAN and manganese(III) acetate towards the oxidation of these carboradical intermediates. Heiba and Dessau[56] reported the order to be 12 : 1 for the relative reactivity of Ce(IV) and Mn(III) in the oxidation of secondary alkyl radicals.

Cyclization to give cyclopentanes with an exo methylene unit

The goal to establish a 'one-flask' method for the synthesis of multi-functional cyclopetanes can be accomplished by use of combination of metal-containing reagents including CAN[20]. Products of this class are valuable synthons in organic synthesis. As shown in Scheme 8, a malonate or a β-keto ester is first treated with allyltrimethylsilane (1.3 equiv) and CAN (2.1 equiv) in acetic acid at 25°C for 4.0 h. Second, $Mn(OAc)_3 \cdot 2H_2O$ (1.1 equiv), $Cu(OAc)_2 \cdot H_2O$ (1.1 equiv), and another portion of allyltrimethylsilane (1.3 equiv) are added to the reaction matrix. After 1.0 h at 80°C, the desired carbocycles possessing an exo methylene unit can be obtained in 61–71% yields. Furthermore, extension of this procedure to the synthesis of the triisopropylsilyl analog is successful by replacement

of the second portion of allyltrimethylsilane with allyltri-isopropylsilane (1.3 equiv, Scheme 8). These reactions go through an intramolecular radical cyclization pathway.

It is essential to use CAN in combination with $Mn(OAc)_3 \cdot 2H_2O$ and $Cu(OAc)_2 \cdot H_2O$ for accomplishment of the sequential allylation, cyclization, and elimination shown in Scheme 8. Application of $Mn(OAc)_3 \cdot 2H_2O$ alone in these reactions leads to cyclopentane derivatives attached by a methyl, instead of methylene, unit.
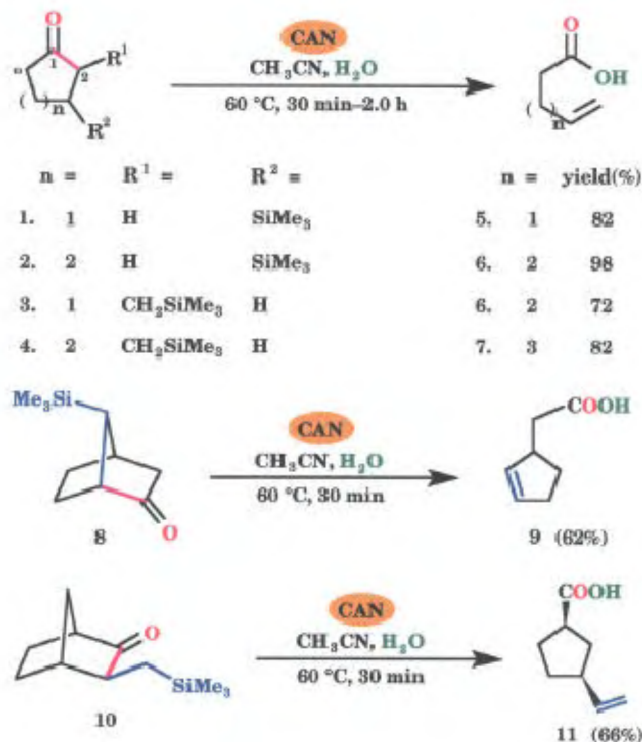
These new methods are successfully developed by use of CAN in methanol or acetic acid[20]. It is not necessary to carry out the reactions under anhydrous conditions. Moreover, products are generated exclusively in good to high yields through the carbon–carbon bond formation. Additional advantages associated with the new methods include that completion of the reaction often requires a short period of time (≤ 4.0 h) and can be noted by the orange colour faded from the solution.
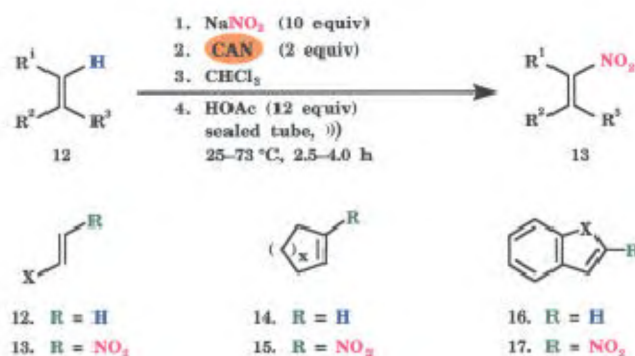
Oxidative fragmentation

The Norrish Type I cleavage of cycloalkanones at the carbon–carbon bonds adjacent to the carbonyl groups gives a mixture of esters and alkenyl aldehydes[57]. For unsymmetric cycloalkanones, regioselectivity may be poor because cleavages could occur at either the C_1–C_2 or the C_1–C_ω bond[58]. These two problems limit applicability of this photochemical reaction in synthetic chemistry despite its unique reaction pattern.

Introduction of a silyl group at a β position of the substrate can solve the regioselective problem of cleaving site[59–63]. The ultimate goal is to allow the reaction to produce a single product, instead of a mixture containing an ester and an alkenyl aldehyde. Application of reagent CAN to the C–C bond cleavage in the C(=O)C–C moiety of β-(trimethylsilyl)cycloalkanones gives ω-alkenylcarboxylic acids as the exclusive product (see Scheme 9, ref. 42).

Oxidation of a carbonyl group to generate the corresponding radical cation through one-electron transfer can be accomplished by use of CAN[64]. Thus treatment β-(trimethylsilyl)cycloalkanones (**1–4**, **8** and **10**) with 2.4 equivalents of CAN in a 50% aqueous acetonitrile solution at 60°C produces ω-alkenylcarboxylic acids (**5–7**, **9**, and **11**) in 62–98% yields (Scheme 9, ref. 42). No by-product is detected through the C_1–C_ω bond cleavage. These reactions are applicable to five- and six-membered cycloalkanones and bicyclic ketones bearing a β silyl group at an endo (i.e. **1**, **2** and **8**) or an exo (i.e. **3**, **4** and **10**) position. The colour change in the solutions from dark brown to pale yellow or colourless indicates completion of the reactions.

n =	R^1 =	R^2 =		n =	yield(%)
1. 1	H	SiMe$_3$	5.	1	82
2. 2	H	SiMe$_3$	6.	2	98
3. 1	CH$_2$SiMe$_3$	H	6.	2	72
4. 2	CH$_2$SiMe$_3$	H	7.	3	82

Scheme 9.

Scheme 10.

Use of CAN in combination with introduction of a silyl group in cycloalkanone substrates allows chemists to accomplish the carbon–carbon bond cleavage with high chemo- and regioselectivity. These reactions give ω-alkenylcarboxylic acids as the single product in good to excellent yields under mild conditions. In comparison with the Norrish Type I cleavage, this new strategy may have a greater potential in synthetic chemistry.

Nitration

Preparation of α,β-unsaturated nitroalkenes from alkenes

Being good Michael acceptors, α,β-unsaturated nitroalkenes are widely applied in organic synthesis[65].

Table 1. Nitration of olefins by use of NaNO$_2$ (10 equiv), CAN (2.0 equiv), and HOAc (12 equiv) in chloroform under sonication at 600 W in a sealed tube to give the corresponding α,β-unsaturated nitroolefins

Alkene	X =	Temp °C	Product	% Yield
12a	Et$_3$SiCH$_2$–	25–55	**13a**	57
12b	i-PrMe$_2$SiCH$_2$–	25–55	**13b**	51
12c	(cyclohexyl)Me$_2$SiCH$_2$–	25–55	**13c**	65
12d	(Me$_2$HCMe$_2$C)Me$_2$SiCH$_2$–	25–55	**13d**	70
12e	(n-Bu)$_3$SiCH$_2$–	25–55	**13e**	72
12f	(n-C$_6$H$_{13}$)$_3$SiCH$_2$–	25–55	**13f**	82
12g	(Me$_2$CHCH$_2$)$_3$SiCH$_2$–	25–55	**13g**	86
12h	(i-Pr)$_3$SiCH$_2$–	25–55	**13h**	81
12i	(EtO)$_3$SiCH$_2$–	25–55	**13i**	53
12j	n-C$_6$H$_{13}$–	25–73	**13j**	99
12k	Ph–	25–73	**13k**	82
14a	1	25–73	**15a**	86
14b	2	25–73	**15b**	99
14c	4	25–73	**15c**	71
16a	O	25–73	**17a**	62
16b	CH$_2$	25	**17b**	54

Among various methods reported for their preparation[66–68], a method involving the use of CAN provides a practical way to the synthesis of α,β-unsaturated nitroalkenes in good to excellent yields (see Scheme 10, refs 25, 26). Reaction of an alkene **12**, **14**, or **16** with sodium nitrite, CAN, and acetic acid in chloroform in a sealed tube at 25–73°C followed by sonication of the reaction mixture produces nitroalkenes **13**, **15**, and **17**, respectively, in good to excellent yields (see Table 1). The substrates include acyclic and cyclic olefins, styrene, indene, benzofuran, and allylsilanes.

Among various solvents applied for the nitration, use of chloroform gives a higher yield of the desired nitro olefins than by others, including water, methanol, acetonitrile, and ethyl acetate. The solubility of CAN is, however, low in chloroform. Consequently application of ultrasound up to 600 W to the heterogeneous solution can efficiently accelerate the reactions.

Nitration of allylsilanes

In 1-nitro-3-organosilyl-1-propenes, the conjugated nitroalkenyl and the allylsilane moieties therein are often labile towards the reaction conditions employed. Jolibois *et al.*[69] reported a method, which is useful in the synthesis of compounds of this class. The conditions associated with the sonochemical method involving the use of CAN (see Scheme 10) are also found mild enough to allow some allylsilanes to be converted to the corresponding α,β-unsaturated nitro olefins[25] (see Table 1, **12a–h**). The nitro group is introduced at the terminal vinylic carbon exclusively. The yields depend upon the size of the silyl groups, such as 81% yield for (i-Pr)$_3$Si and 86% yield for (i-Bu)$_3$Si; a bulkier group of-

ten gives a higher yield. This nitration method is limited to the preparation of allylsilanes bearing a small silyl group, including Me$_3$Si, EtMe$_2$Si, Ph$_2$MeSi, and (MeO)$_3$Si because of the competing desilylation process.

Several advantages are associated with the sonochemical method for the synthesis of α,β-unsaturated nitroalkenes by use of sodium nitrite, acetic acid, and CAN. These include mild and non-anhydrous reaction conditions, high regioselectivity, good to excellent yields, and a short reaction time.

Removal of protecting groups

The chemistry of protecting groups on amino acids and nucleic acids is of high importance to the industry of protein and gene chips. Recently, CAN has been developed as an efficient reagent for removal of commonly used protecting groups.

Deprotection of the tert-butoxycarbonyl group

One of the most commonly used protecting groups for amino acids in peptide synthesis is the *tert*-butoxycarbonyl (*t*-BOC) group[70,71]. Reagent CAN acts as a catalyst for removal of the *t*-BOC group from organic compounds under neutral conditions (Scheme 11, ref. 34). Treatment of a *t*-BOC containing compound (i.e. **18a–23a**) in acetonitrile with 0.20 equivalent of CAN upon heating at reflux gives the deprotected products (i.e. **18b–23b**) in 90–99% yields. This deprotection procedure is applicable to compounds bearing a *t*-BOC group attached to a nitrogen atom (i.e. **18a–20a**),
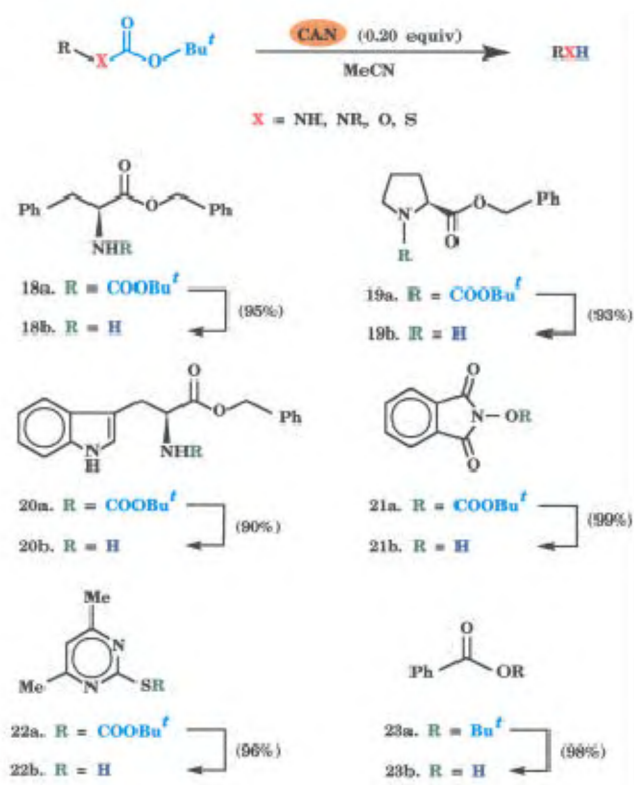
Scheme 11.

an oxygen atom (i.e. **21a**), or a sulfur atom (i.e. **22a**). By use of the same method, debutylation also occurs in ester **23a** to afford the corresponding acid **23b** in 98% yield. At 25°C, the same deprotection also proceeds; yet a longer reaction time (38–48 h) would be required.

The functionalities remained intact under the conditions, involving the use of CAN including benzyl esters as well as indole, pyrimidine, and phthalimide nuclei. The value of this method is that undesired racemization in amino esters does not take place.

Deprotection of the triphenylmethyl and the monomethoxytrityl groups

Functioning as a one-electron transfer agent[5,64], CAN acts as a suitable catalyst for efficient detritylation of nucleosides and nucleotides. Other reagents applied for removal of the trityl group include hydrogen chloride, hydrogen bromide, acetic acid, trifluoroacetic acid, sodium in liquid ammonia, hydrogen gas along with Pd/C, chlorine gas, etc. Performance of detritylation with these reagents may give by-products, cause cleavage of nucleobases in nucleosides and nucleotides, destroy other functional groups therein, or be limited in a small scale reaction.

Examples shown in Scheme 12 show that the triphenylmethyl (trityl) and the monomethoxytrityl

(MMTr) protecting groups in various nucleosides and nucleotides can be removed by a catalytic amount of CAN (0.10 equiv)[33]. These reactions can be performed in a wet mixture of acetonitrile and DMF at 25°C. The yields range from 80–98% for the desired products.

Some protecting groups sensitive to acids survive under the conditions involving the use of CAN[33]. These groups include (dimethylamino)methylidene, *tert*-butyldimethylsilyl, and isopropylidene. The *N*-glycosidic bond of nucleosides and nucleotides as well as the phosphoramidate linkage also remains intact during detritylation by use of CAN. Removal of the MMTr group from 5′-*O*-mono(*p*-methoxy)trityl adenosine proceeds about 10 times faster than that of the trityl group from 5′-*O*-trityl adenosine[72].

Furthermore, the acyl group in esters survives and yet its migration to the adjacent hydroxyl group would not occur in the conversion of 1-benzoyl-3-(triphenyl-methyl)glycerol to 1-benzoylglycerol (94–98%) by use of CAN (Scheme 13). In contrast, treatment of 1-benzoyl-3-(triphenylmethyl)glycerol with 5% CF_3CO_2H in acetonitrile gives a mixture of 1-benzoylglycerol, 2-benzoylglycerol, and glycerol in a ratio of 1.5 : 1 : 2.5.

Deprotection of the tert-butyldimethylsilyl group

The *tert*-butyldimethylsilyl (TBDMS) group is widely applied in protection of the hydroxyl functionality in organic synthesis[73,74]. Its selective removal from the corresponding silyl ethers with different steric environment in nucleosides may not be accomplished by commonly used reagents, such as HF in aqueous MeCN, Bu$_4$NF in THF, and clay in aqueous MeOH[29].

For the TBDMS-containing-compounds **24a–f**, **26**, **28**, and **30**, use of 0.85 equivalent of CAN in 2-propanol allows selective deprotection to take place at 25°C to give products **25a–f**, **27**, **29**, and **31**, individually, in 85–95% yields (Scheme 14, ref. 29). These reactions comprise deprotections occurring to 2′,5′-disilylated, 3′,5′-disilylated, and 2′,3′,5′-trisilylated nucleosides (i.e., **24a–f**), disilylated ascorbic acid **26**, siloxymethyl phenol ether **28**, and silylated amino ester derivative **30**.

The TBDMS group in a secondary ether virtually remains intact under the conditions involving CAN. Although the adjacent migration of the 2′- and the 3′-*O*-TBDMS groups of ribonucleosides is reported in MeOH or pyridine[75], such a migration does not take place in **25a**, **25b**, **27**, and **29** under the conditions involving CAN[29]. Furthermore, the TBDMS group can also be removed selectively in the presence of a *tert*-butoxycarbonyl functionality (see **30a** → **31**). Proper choice of 2-propanol as the reaction media is the key to the success of the selective desilylation. Use of methanol, ethanol, or 1-propanol as the solvent results in the deprotection of all TBDMS groups.
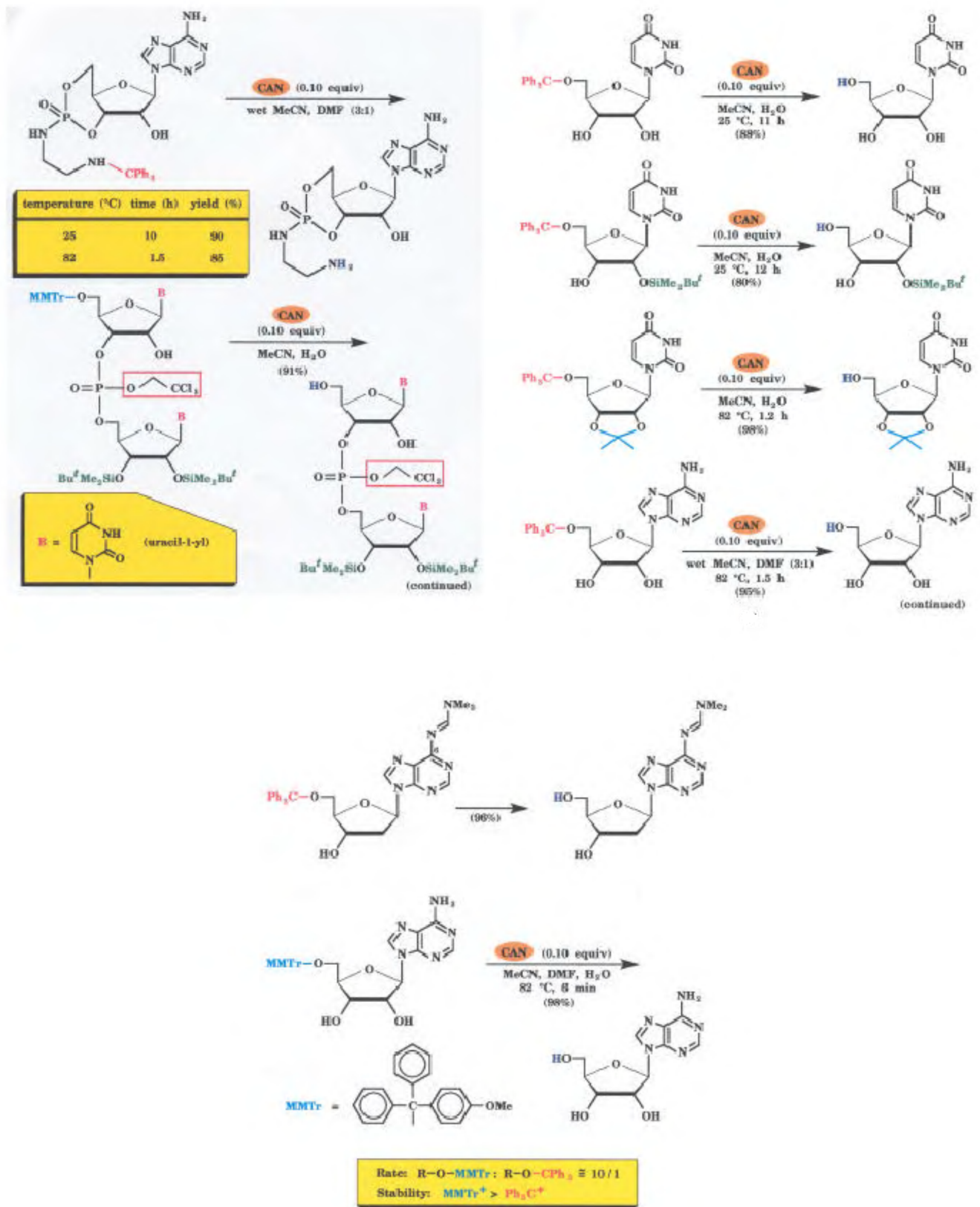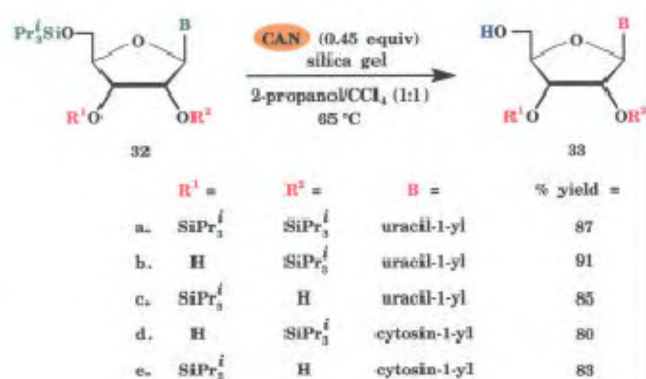
Scheme 12.
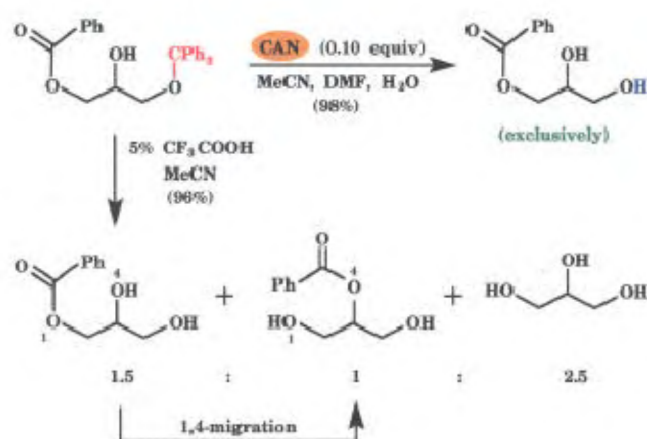
Scheme 13.
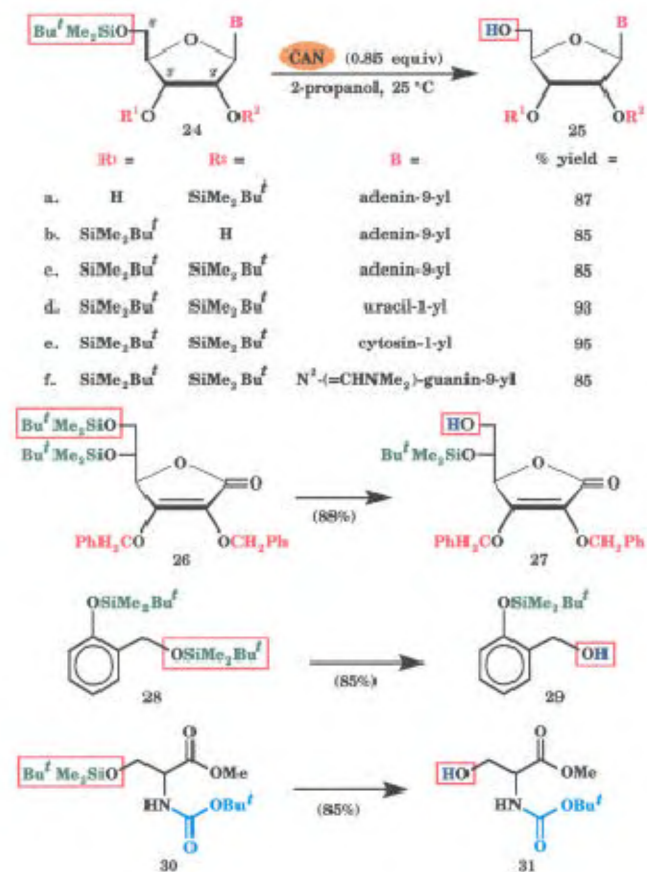
Scheme 14.

Deprotections of the triisopropylsilyl group with silica gel impregnated ceric ammonium nitrate

In contrast to the TBDMS group, the triisopropylsilyl (TIPS) group cannot be removed from nucleosides **32a–e** by use of a catalytic amount of CAN. A solution to this problem is to use silica gel impregnated CAN[29]. This mixture functions as an effective reagent for
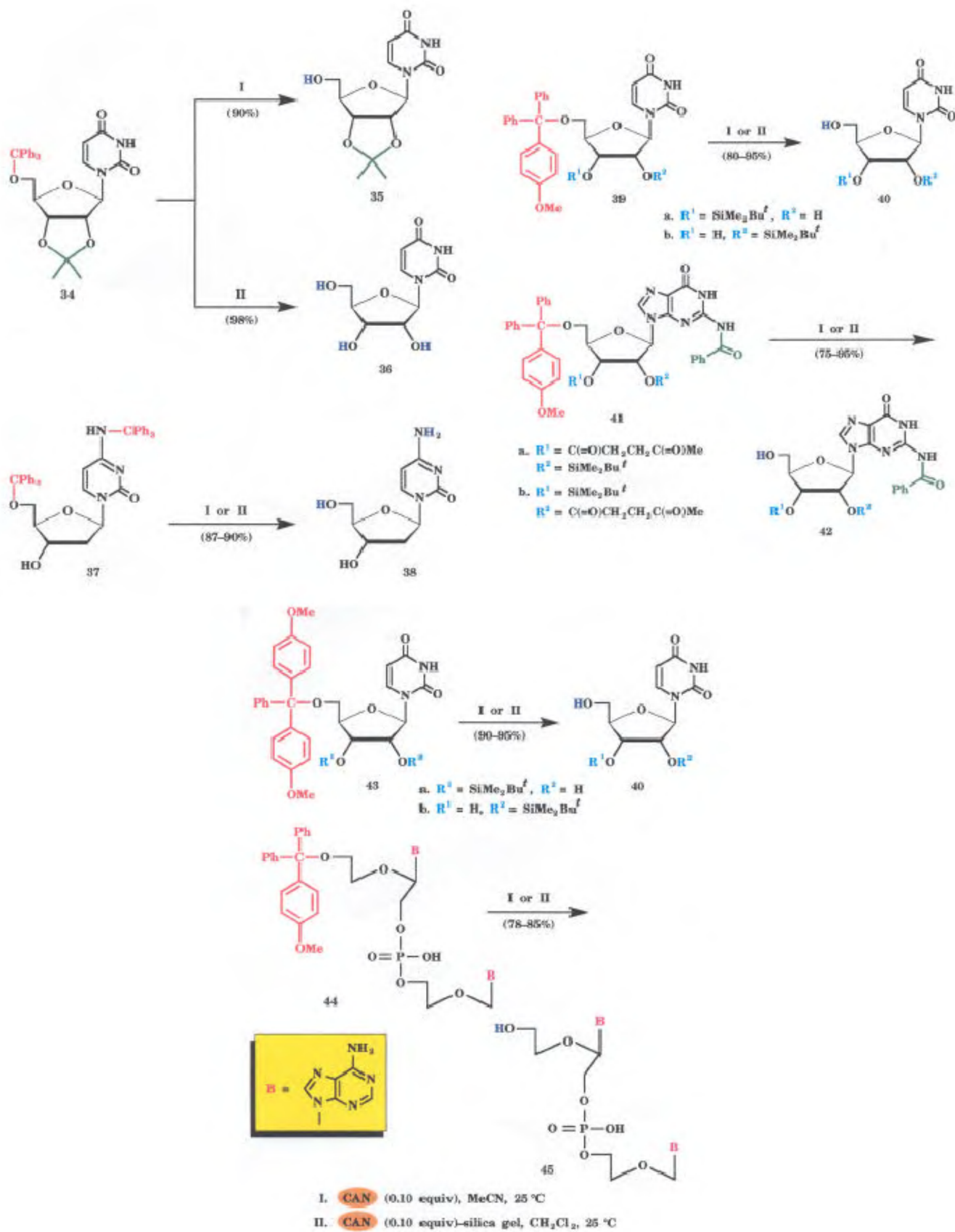

Scheme 15.

removal of the TIPS functionalities from a variety of ribonucleoside substrates as shown in Scheme 15. Treatment of various silylated compounds **32a–e** with 0.45 equivalent of silica gel supported CAN in a mixture of 2-propanol and CCl_4 in a 1 : 1 ratio at 65°C for 1.5–28 h produces the desired products **33a–e** in 80–95% yields. In these reactions, the TIPS group in primary silyl ethers moieties is selectively removed.

This new method is found applicable to silylated adenosine, uridine, guanosine, and cytidine[29]. Their nucleobases do not interfere with the electron transfer processes between cerium species and the substrates. Acidic deprotection of the TIPS group is much easier than the TBDMS group[76]; yet by use of CAN–SiO_2 allows removal of the TBDMS functionality faster than removal of the TIPS group. For example, the *tert*-butyldimethylsilyl derivative **30** is readily converted to desilylated product **31** in an excellent yield by use of CAN–SiO_2, yet the corresponding triisopropylsilyl derivative of **30** fails to produce **31** under the same reaction conditions[29].

Efficiency of CAN vs CAN–SiO_2 in deprotections

Silica gel can bring the catalyst CAN and substrates containing a *tert*-butoxycarbonyl, trityl, or a silyl group into proximity by adsorption[77,78]. Accordingly, the electron transfer process between reactants is facilitated and the deprotection process can proceed much faster. In addition to the TIPS group, CAN adsorbed on silica gel functions as an effective reagent for removal of the trityl, monomethoxytrityl, and dimethoxytrityl functionalities from a variety of ribonucleoside substrates shown in Scheme 16 (ref. 29). Being rapid and selective, this procedure allows the conversion of substrates to the parent alcohols or amines in good to excellent yields. These outcomes broaden the applicability of these protecting groups in the field of nucleoside chemistry and, in potential, gene chip industry.

Scheme 16.

Table 2. Comparison of the efficiency for detritylation of protected nucleosides by use of CAN (0.10 equiv) in MeCN or silica gel-supported CAN (0.10 equiv) in CH_2Cl_2 at 25°C

Starting material	Time (h)		% Yield by isolation		Product
	CAN	CAN–SiO$_2$	CAN	CAN–SiO$_2$	
34	10	–	90	–	**35**
34	–	1.5	–	98	**36**
37	15	2.0	87	90	**38**
39a	1.5	0.10	80	90	**40a**
39b	1.25	0.10	85	95	**40b**
41a	1.5	0.10	80	90	**42a**
41b	1.2	0.10	75	95	**42b**
43a	0.15	0.01	90	92	**40a**
43b	0.10	0.01	90	95	**40b**
44	1.0	0.10	78	85	**45**

Results summarized in Table 2 indicate efficiency by use of CAN–SiO$_2$ (containing 0.10 equivalent of CAN) in comparison with CAN alone during detritylation of protected nucleosides and nucleotides in dichloromethane at 25°C (ref. 29). The deprotection reactions often go much faster and produce the same products in higher yields when the CAN–silica gel reagent is used (i.e., Method II) to replace CAN. The only different results in these two methods come from the conversions of **34** → **35** by CAN and **34** → **36** by CAN–SiO$_2$; in the latter reaction, the isopropylidene group in **34** is removed (Scheme 16 and Table 2).

Stability of the resultant carbocationic species follows the order DMTr$^+$ > MMTr$^+$ > Tr$^+$ (DMTr = p-dimethoxytrityl). Their stability influences efficiency of deprotections by use of CAN. Under the same conditions, the deprotection of 5′-O-DMTr nucleosides proceeds about 10 times faster than the deprotection of 5′-O-MMTr nucleosides (Table 2)[29]. Moreover, the deprotection of 5′-O-MMTr nucleosides proceeds about 10–20 times faster than deprotection of 5′-O-Tr nucleosides. Thus deprotection reactions by utilization of CAN–SiO$_2$ indicates a remarkable increase in the rate of the reactions involving a solid support.

Conclusions

Being a versatile chemical agent, CAN has been applied to organic reactions in catalytic or stoichiometric amounts. Our research group has succeeded in using CAN to perform allylation, cyclization, oxidative fragmentation, nitration, as well as removal of *tert*-butoxycarbonyl group, trityl group, and *tert*-butyldimethylsilyl group. Furthermore, use of silica gel impregnated CAN can effectively initiates the deprotection of triisopropylsilyl group. Because the reagent CAN can be manipulated easily and is cost effective, we believe that many new chemical reactions will be developed involving the use of this reagent in the near future.

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