Sodium perborate and sodium percarbonate: further applications in organic synthesis

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Covering 1995 to 1998.

1   Introduction

1.1   Earlier reviews

The versatility of sodium perborate (SPB) and sodium percarbonate (SPC) in functional group oxidations has been highlighted in two previous reviews in 1995,[1,2] covering between them nearly one hundred papers on useful oxidations. Ref. 1, by the present authors, also described the basis of the chemistry of these two peroxygen compounds (Fig. 1), which is distinct in several respects. In ref. 2, Muzart considered the mechanisms of some of the main types of oxidation, including some metal-catalysed reactions.

Since these two reviews were prepared, more than fifty further papers on the use of these two compounds in oxidations have appeared, including many on metal-catalysed systems. The present article surveys this new information, almost all of it from the period 1995–1998.

Also published since the previous reviews are a concise account of general chemistry of inorganic peroxides, including SPB and SPC,[3] and a Chinese review of some applications of SPB in synthesis.[4]

1.2   Brief summary of SPB and SPC chemistry

In water, or in solvents with a significant aqueous component, both persalts function mainly as a convenient source of mildly alkaline hydrogen peroxide. SPB is a convenient source of such H_2O_2, the borate helping somewhat to buffer, stabilise against

decomposition, and activate towards nucleophilic oxidations, through associated species such as $[B(OH)_3(OOH)]^-$. SPC is slightly more alkaline, and solutions can contain minor amounts of a "true" percarbonate species, $[HOOC(O)O]^-$, which is electrophilic in character.

SPB is a cyclic disubstituted peroxide, and only dissolves significantly in those non-aqueous media with which it reacts. It is often used in acetic acid or other carboxylic acids. Active oxidants formed would appear to be peracids and their anions, which show both nucleophilic and electrophilic properties. In contrast, SPC is simply a peroxyhydrate, and acts as a source of anhydrous H_2O_2. The H_2O_2 can be leached out by non-aqueous media in which it dissolves and ultrasound assists this process. Carboxylic anhydrides or other acylating agents, rather than acids, are needed to form peracids with SPC, even under anhydrous conditions.

A fuller description and explanation is given in ref. 1.

2   Oxidations using SPB and SPC

2.1   Thiols, sulfides and selenols

Many recent papers confirm the controllability and chemoselectivity of the SPB–acetic acid system for sulfide oxidation. Oxidation of chiral sulfides to sulfoxides has been reported by Bower *et al.*,[5] as exemplified by conversion of **1** into **2** in 94% yield (Scheme 1).[5] Unfortunately the de was only 18%, and better results were obtained with the TBHP–VO(acac)$_2$ system (TBHP = *tert*-butyl hydroperoxide), which interacts more strongly with the neighbouring chiral group. This contrasts with Ohta and co-workers earlier work[6] (see also ref. 1).
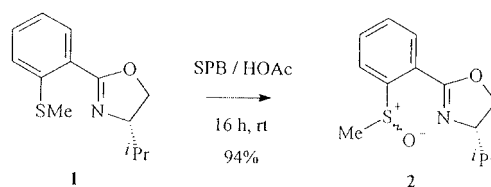
Scheme 1

Yue *et al.* found[7] that sulfides could be oxidised selectively to sulfoxides or sulfones in the presence of nitrile groups by careful, stepwise addition of SPB in acetic acid, as shown for **3**→**4** (Scheme 2). Perborate has been used to perform this same type of oxidation in a multi-stage synthesis of barbaralanes, in which the bis(vinyl sulfide) (**5**, X = S) derived from Meerwein's ketone is oxidised to the bis(vinyl sulfone) (**5**, X = SO$_2$) by SPB–acetic acid, taking advantage of the much greater ease of oxidation at sulfur than at the alkene bonds.[8]
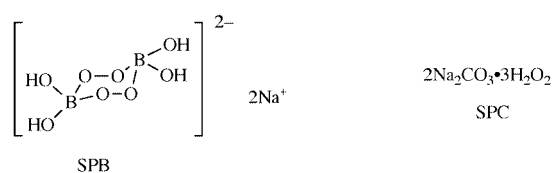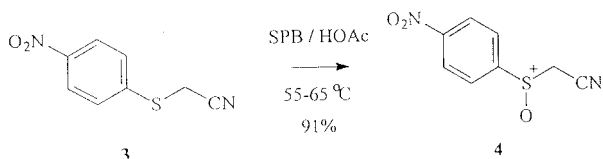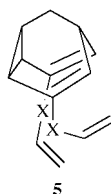
Fig. 1

Scheme 2

5

Although oxidation at sulfur is normally relatively easy, *S*-arylthioacetic acids are said to undergo cleavage preferentially when treated with SPB in acid medium, to give thiophenols as products; the reaction kinetics have been studied.[9,10] The same substrates have been used to study the kinetics of molybdate-catalysed oxidation by SPB in aqueous acetic acid; here, the active species appears to be a molybdenum peroxo species, the persalt simply acting as an H_2O_2 source.[11]

Preparation of 2-chlorobenzimidazoles by treatment of the corresponding 2-sulfonic acids with PCl_5–$POCl_3$ has been recommended as a method of choice, and the sulfonic acids are best and most safely prepared on a large scale by oxidation of benzimidazole-2-thiones with aqueous SPC, **6**→**7** (Scheme 3).[12] Yields are excellent, and the reactions can be carried out on multi-hundred gram scale.

$R^1 = R^2 = H, 85\%$

$R^1 = Cl, R^2 = H, 83\%$

$R^1 = R^2 = Cl, 92\%$
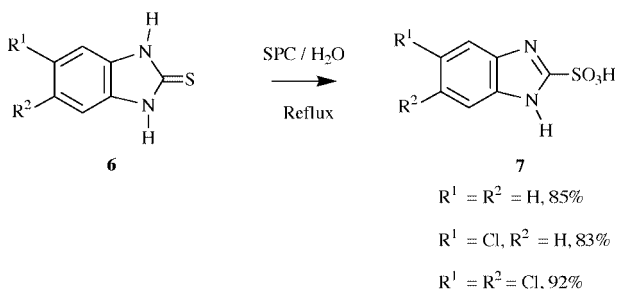
Scheme 3

A convenient method for preparation of diphenyl diselenide by oxidation of selenophenol with air in the presence of SPC has been reported.[13]

2.2 Amines, imines, *N*-heterocycles, oximes, hydrazones and C–N coupling

Two kinetic studies have been published recently on aniline oxidation using catalysed SPB systems in aqueous acetic acid, the catalysts being hexacyanoferrate(III)[14] and Mo or W(VI) compounds.[15] The product is azobenzene, but the methods are almost certainly of no synthetic significance. It has been claimed that a polymer-supported perborate has been prepared from a strong base ion-exchange resin, and used to oxidise aniline to nitrobenzene in 90% yield.[16] Oxidation of 3-amino-1,2,4-triazoles by SPB can be carried out selectively to give 3-nitro-1,2,4-triazoles.[17]

Nongkunsarn and Ramsden have successfully used SPB in trifluoroacetic acid (a stronger alternative to the usual acetic acid system) for oxidation of several *C*-aryl or -alkyl *N*-aryl-aldimines to *N*,*N*-disubstituted formamides, *e.g.* **8**→**9** (Scheme 4).[18] Yields are generally in the range 50–60%, and reaction is postulated to proceed through oxaziridine formation, followed by cleavage of the O–N bond.

The efficacy of several reagents, including SPB–HOAc, for
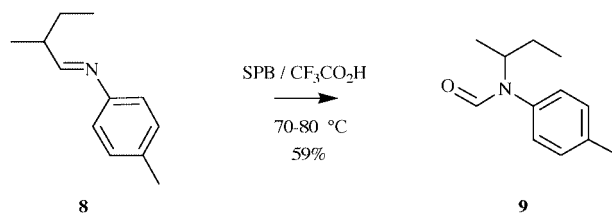
Scheme 4

N-oxidation of four 3-substituted pyridines was compared by Bremner and co-workers.[19] They concluded that MCBPA was best overall. This is not surprising, since the most likely active species for this type of oxidation in the SPB system is peracetic acid, which is produced indirectly (ref. 1, p. 6149) and is less electrophilic than MCPBA. The substitution of trifluoroacetic for acetic acid was not tried during this study.

[15]N-Labelled trimethylpyrazine could be oxidised to a mixture of 1-, 4- and di-*N*-oxides by SPB in acetic acid.[20]

In a study of *N*-hydroxylation of azoles using MCPBA, H_2O_2–formic acid, or SPB in pivalic acid, the last of these was found to be superior to MCPBA in the preparation of *N*-hydroxytetrazoles, *e.g.* **10**→**11** + **12** (Scheme 5), though the pre-formed peracid was better in all other cases (mono-, di- and triazoles).[21] The pivalic acid system is expected to be the least acidic of the three, and milder than SPB–acetic acid, which may be important here.
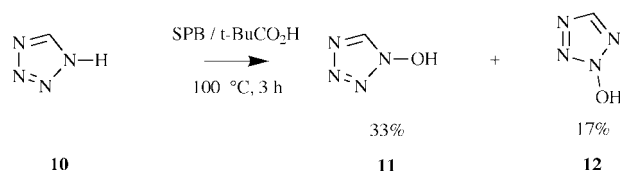
Scheme 5

Bandgar *et al.* have published further on the conversion of oximes to carbonyl compounds, **13**→**14** (Scheme 6).[22] Ten examples in all were studied and lower yields are obtained for the aldehyde cases, presumably due to further oxidation to the acids under the reaction conditions. Bandgar has also described a very closely related transformation, namely the regeneration of aldehydes and ketones from their semicarbazones using SPB.[23]
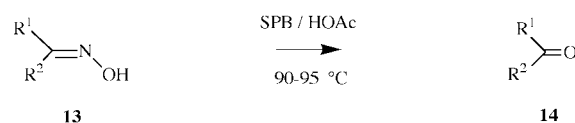

$R^1, R^2 = $ Cyclopentyl, 89%, 8 h

$R^1, R^2 = $ Ph, 87%, 5 h

$R^1 = 4$-BzOPh, $R^2 = $ Me, 75%, 3 h

Scheme 6

A comparative study of aqueous hydroxylamine oxidation by H_2O_2 and SPB concluded that the latter is faster at high concentrations, and is catalysed further by Cu(II) addition.[24] It is not surprising that SPB and H_2O_2 only differ at high concentrations, since in more dilute solutions the SPB is substantially hydrolysed to free H_2O_2.[1]

In a recent synthesis of chiral 4-hydroxyisoxazolines (Scheme 7),[25] SPC performs two actions, one of which is the slow conversion of hydroximic acid halide to nitrile oxide, which then undergoes [3 + 2] cycloaddition with a vinylboronic ester. The product is then cleaved oxidatively to the hydroxy compound by SPC. The 4-hydroxy-Δ^2-isoxazolines **15** (Scheme 7) can be
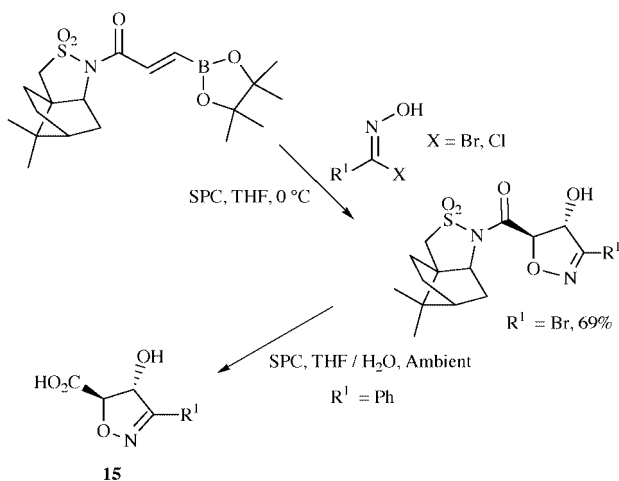
Scheme 7

prepared in this way in a "one pot" procedure. Four examples gave overall yields of 68 to 87% and the products were isolated as the methyl esters.

Finally, SPC has been used by Boulouard *et al.* in a synthesis of pyrrolothieno[1,4]diazepines, as illustrated by **16→17** (Scheme 8).[26]
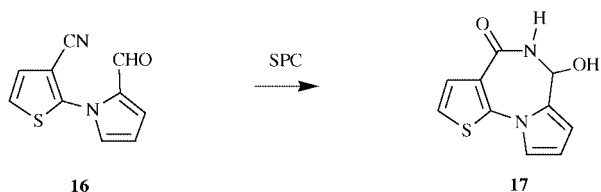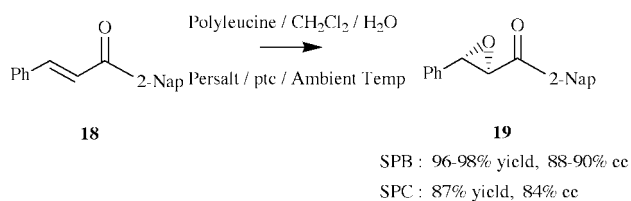
Scheme 8

2.3 Olefins, C–C cleavage and aromatic side chains

Hou and Tao have published a further paper on epoxidation of a wide range of alkenes with SPB or SPC in Ac$_2$O–CH$_2$Cl$_2$.[27] The effectiveness of acetic anhydride with perborate for electrophilic epoxidations contrasts the behaviour of acetic acid, and is probably due to the more rapid formation of peracetic acid. Care is suggested in the use of these systems, as the potential formation of hazardous diacyl peroxides has not been fully explored.

Roberts' group has explored in some detail extension of the Julia asymmetric epoxidation reaction to enones other than chalcones.[28] This is an alkaline peroxide oxidation, where SPB and SPC are both good choices as previously noted. In the presence of polyleucine as catalyst, excellent yields and good ee values have been obtained, *e.g.* **18→19** (Scheme 9). Virtually the same approach, but with the added effect of 7 hours of sonication of a variety of chalcones, has given, again, excellent yields of epoxides, but the ee values were somewhat lower than those obtained in the Roberts study.[29]

Scheme 9

SPB : 96-98% yield, 88-90% ee
SPC : 87% yield, 84% ee

Two recently-published patents[30,31] refer to SPB and SPC in a list of many oxidants for epoxidation of pyronenes as precursors for vitamin A, PVC stabilisers, or epoxy resin modifiers.

However, no examples of use of persalts as oxidants are given in either patent, and there is therefore some doubt as to whether these were in fact employed.

A more familiar use for SPB–acetic acid is represented by the conversion of 1,2,3,6-tetrahydropyridine-1-carboxylates to *trans*-4-acetoxy-3-hydroxypiperidine-1-carboxylates, by addition across the double bond.[32] The products are intermediates in the preparation of 3-hydroxyfentanyl analgesics. Continuing with dihydroxylation and equivalents, a recently-published patent describes the dihydroxylation of 1,2,3,6-tetrahydrophthalic acid with H$_2$O$_2$ or persalts without a catalyst, followed by cleavage of the diol in the presence of various metals, notably tungstate.[33]

Kabalka's group has recently published a method for dibromination of alkenes using a mixture of sodium bromide and SPB in acetic acid.[34] Yields in 9 examples range from 72–90%, and the reactions proceed smoothly under mild conditions at room temperature.

Other cleavage reactions feature the oxidative decarbonylation of β-aryl- and β-heteroaryl-pyruvic acids by SPB, described by Ramsden *et al.*[34,35] This is believed to proceed *via* (nucleophilic) epoxidation of the enol tautomer, followed by decarboxylation (*e.g.* **20→21**) (Scheme 10).
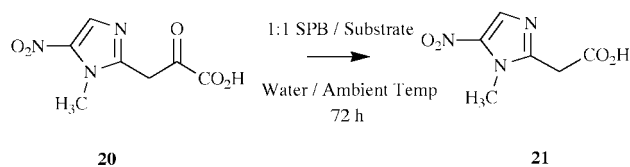
Scheme 10
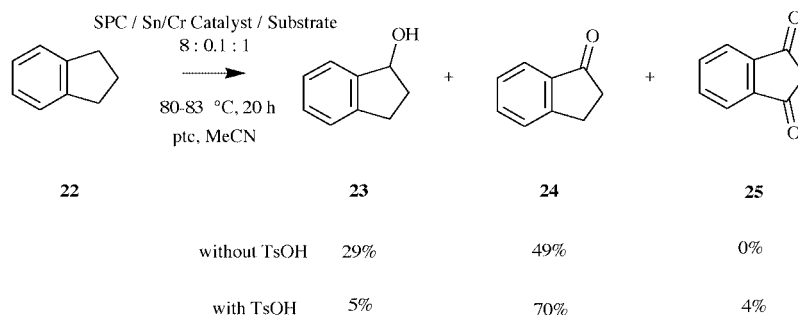
Kabalka's group has used SPC for oxidative cleavage of α-haloketones[36] and α-ketols or α-diketones[37] to carboxylic acids, assisted by ultrasound. Typical conditions for the former reaction are sonication of acetone–water solutions at ambient temperature for 1 hour, which gives, for example, an 85% yield of 4-nitrobenzoic acid from α-bromo-4-nitroacetophenone. This compares with 60% in 5 hours conventional heating at 60 °C, and similar improvements were seen with other substrates. A 5:1 stoichiometric ratio of SPC to substrate was used for the α-haloketones, increased to 15:1 for the ketols and diketones.

Carbon–carbon cleavage in catechols, using H$_2$O$_2$ or SPC, is catalysed by, for example, iron sulfophthalocyanines, the products being maleic acids.[38] This chemistry is suggested as a potential method for treatment of phenolic effluents.

It is well-known that benzylic oxidations can be catalysed by cobalt acetate in the presence of bromide ion in acetic acid as solvent, using either air or hydrogen peroxide as the oxidant. Better selectivity to aldehyde can be obtained with the latter, and a further improvement has been demonstrated when SPB is used as the H$_2$O$_2$ source.[39] For example, 4-*tert*-butyltoluene can be oxidised to 4-*tert*-butylbenzaldehyde with 75% selectivity in 3 hours at 50 °C with perborate "monohydrate", compared to 40% with H$_2$O$_2$ under the same conditions. As well as minimising generation of molecular oxygen by controlling the release of oxidant, the SPB helps maintain the catalyst activity owing to its low water content.

Benzylic oxidations can also be carried out by the chromium-catalysed SPC system developed for alcohol oxidation in Muzart's group.[40] Preliminary work showed that indane gave indan-1-one as main product, **22→24**, with the 1-ol, **23**, and 1,3-dione, **25**, also being formed (Scheme 11). Tetralin† similarly gave mainly 1-tetralone,† and acyclic side chains are also typically oxidised beyond the alcohol, as expected.

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† The IUPAC name for tetralin is 1,2,3,4-tetrahydronaphthalene and for 1-tetralone is 3,4-dihydronaphthal-2(1H)-one.

SPC / Sn/Cr Catalyst / Substrate
8 : 0.1 : 1

80-83 °C, 20 h
ptc, MeCN

	22	23	24	25
without TsOH		29%	49%	0%
with TsOH		5%	70%	4%

Scheme 11

Chromium catalysts used were PDC (pyridinium dichromate) and the oxide (n-Bu₃SnO)₂CrO₂. The latter appears to be more soluble in the reaction media (DCM or acetonitrile).

2.4 Phenols, alcohols, aldehydes, ketones and nitriles

No new synthetic reactions involving phenols have been reported since the last reviews.[1,2] Ref. 34, discussed in the previous section, concerned catechol oxidation, but was aimed more at destruction of aromatics rather than being a synthetic method.

Regarding alcohol oxidations, Muzart's group has recently added to their previously-published, chromium-catalysed, method a new one based on molybdenum catalysis. SPC is used in dichloroethane or acetonitrile at reflux for 9–24 hours, with MoO₂(acac)₂ and a phase-transfer catalyst.[41] The active species is probably a metal-peroxo complex and, in common with other methods based on Mo and W catalysis, secondary, allylic and benzylic alcohols react more quickly and give higher yields of carbonyl products than primary aliphatic alcohols. For example, in 24 hours 1-phenylpropan-1-ol gives an 85% isolated yield of the aldehyde, whereas hexadecan-1-ol gives 53% aldehyde and 10% acid. Cinnamaldehyde gives, in 9 hours, 63% aldehyde, 24% epoxide and 9% acid.

A study of various other metal catalysts for indan-1-ol oxidation by SPC has also been undertaken by Muzart *et al.* Pd, Rh and Ru chlorides are effective, though none compared favourably with the MoO₂(acac)₂ catalyst.[42]

A kinetic study of oxidation of the enediol L-ascorbic acid in aqueous acid has been carried out, using SPB or perdisulfate.[43] Under these conditions the active oxidant from SPB is likely to be free H₂O₂ rather than any boron species.

SPC has been used in the Dakin and Baeyer–Villiger reactions, and in a recent study, catechol was prepared either from salicylaldehyde or from 2-hydroxyacetophenone. In a similar comparison, quinol was obtained in 66% yield from 4-hydroxyacetophenone, but in only 35% yield from 4-hydroxybenzaldehyde.[44] In another study, a "supported perborate" on strong-base ion-exchange resin was used to oxidise benzaldehyde to benzoic acid in 92% yield.[16] It is unlikely that the predominant anion is [B₂(O₂)₂(OH)₄]²⁻ as in SPB itself.

Baeyer–Villiger oxidation of ketones using persalts and acetic anhydride has been further studied by Tao *et al.* SPC is said to perform very well for cyclic ketones, with yields of lactones being typically 80%, but aromatic ketones only give good yields if the ring is activated. Reactions are assisted by ultrasound.[45] SPB similarly gives good yields of lactones from cyclic ketones when used with acetic anhydride.[46] Attention is drawn to safety comments in the previous section. A further system for Baeyer–Villiger oxidations is described in Section 2.6.

A few patents have recently appeared on various Baeyer–Villiger oxidations which include reference to use of SPB and/or SPC. Nippon Steel claim SPB and formic acid as an inexpensive reagent, and as a more easily-handled alternative to peracetic acid or MCPBA, for lactone manufacture.[47] BASF

claim oxidation of 2-alkoxyethylcyclohexanone to the lactone of 8-alkoxy-6-hydroxyoctanoic acid with SPB–HOAc, (**26→27**, Scheme 12) for onward conversion to lipoic acids.[48]

SPB / HOAc 50% excess

Reflux, 1 h
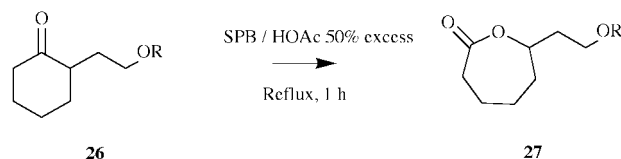
Scheme 12

Hoechst claim the production of halogenated benzoic acids by Baeyer–Villiger oxidation of appropriately halogenated benzophenones. For unsymmetrical benzophenones, the more electron-rich ring migrates, the more electron-poor one retaining the carbonyl function, *e.g.* **28→29** (Scheme 13).

1. SPC / CF₃CO₂H

Ambient, 16 h

2. Hydrolyse

76%
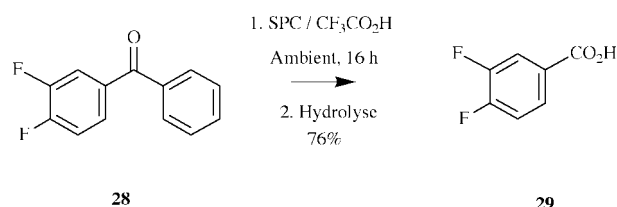
Scheme 13

As in several other patents, SPB and SPC are among a number of oxidation methods listed.[49]

Hydrolysis of nitriles to carboxylic acids has been studied recently by Berlan *et al.* under heterogeneous conditions (no solvent), comparing SPB with copper and cobalt salt catalysts.[50] Reactions are carried out in closed vessels at 240 °C for 1 hour, using conventional or microwave heating, and yields of 70% or over are obtained for many nitriles. For SPB (used at >4:1 molar excess), the first step in the hydrolysis would appear to be the known alkaline peroxide-mediated hydrolysis of nitriles RCN to amides RCONH₂, after which the hot alkaline conditions complete the hydrolysis of amide to acid. It must be stressed that peroxygen systems should not be heated under confinement without at least confirming that the vessel will withstand the pressure resulting from sudden, complete decomposition.

2.5 Organoboranes, iodoarenes and organophosphorus compounds

Sodium perborate has become established as a convenient source of hydrogen peroxide in the workup stage of the classical hydration of olefins *via* hydroboration. This has been mainly due to the work of Kabalka's group, and several further papers have appeared recently.

Primary alcohols can be prepared selectively from terminal alkenes in the presence of ketone and aldehyde groups by hydroboration followed by SPB oxidation.[51] For example, 5-

methylhex-5-en-2-one is converted into 6-hydroxy-5-methyl-hexan-2-one, and undec-10-enal to 11-hydroxyundecanal, as shown in Scheme 14, using dicyclohexylborane formed *in situ* from BH_3–THF and cyclohexene. Terminal alkynes are similarly transformed into aldehydes.[52]
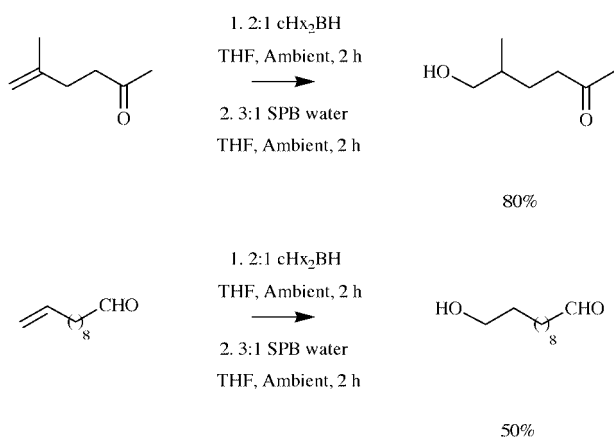
Scheme 14

The same general approach has been used to prepare (+)-isopinocampheol stereospecifically from (+)-α-pinene in 92% overall yield.[53]

A route to alkylarylcarbinols from α,α-dichlorotoluenes and trialkylboranes also uses SPB in the work-up for oxidative cleavage of the organoborane.[54–56] The same overall transformation can be effected using the corresponding benzaldehyde trisyl-[57] or tosylhydrazone[58] as the source of the aryl moiety, with yields generally being superior with the trisyl series. (Scheme 15).
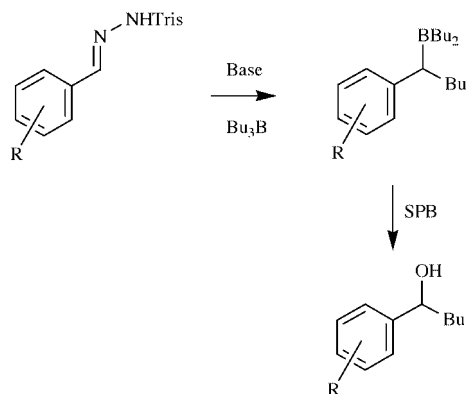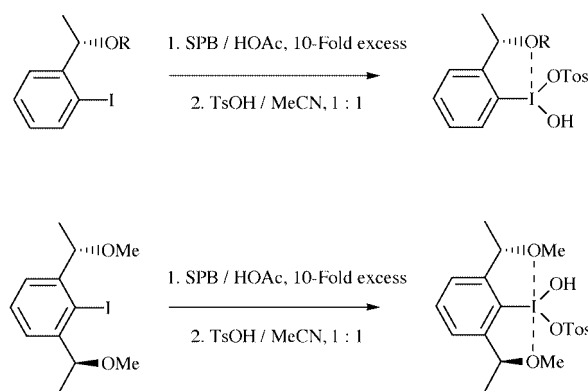

Scheme 15

Turning to iodine oxidation, diacyloxyiodoarenes can be prepared *via* the corresponding iodoarene diacetate (made from iodoarene and SPB–acetic acid) by heating with the appropriate acid and distilling off acetic acid.[59] This provides a convenient source of [bis(1-adamantylcarbonyloxy)iodo]arenes, which can be used to effect nucleophilic (Minisci-type) radical substitution of adamantyl groups in azines, and adamantyl radical addition to electron-deficient olefins.[60] The SPB–HOAc system has also been used in the preparation of various chiral hypervalent iodine compounds (Scheme 16).[61]

Two recent papers from Karunakaran and Muthukumaran describe the kinetics of iodide oxidation by aqueous perborate, catalysed by tungstate[62] and molybdate.[63] It was, however, recognised that in these systems the SPB is essentially a source of H_2O_2.

The sole recent reference to phosphorus compound oxidation is a Bayer patent,[64] which describes the oxidation of *S,S,S*-tributyl phosphorotrithioate from tributyl phosphorotrithioite using SPB or SPC at 40–65 °C and pH 6–12.
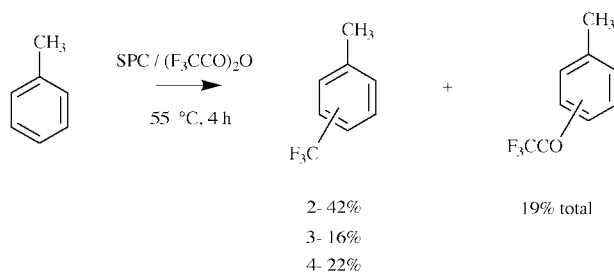

Scheme 16

2.6 Miscellaneous

SPC has been shown to be an effective and convenient oxidant for *in situ* generation of trifluoroperacetic acid in a buffered anhydrous system, suitable for Baeyer–Villiger reactions, *etc*. Addition of trifluoroacetic anhydride to a suspension of SPC in DCM at ambient temperature in the presence of ketones gave good yields of esters, *e.g.* 6-phenylhexan-2-one was converted into 4-phenylbutyl acetate in 2 hours.[65] This has distinct advantages over the classical TFPAA generation from high strength (85–90%) H_2O_2, where reverse addition (peroxide to anhydride) is required owing to the water content of the mixture, and the resulting strong acid mixture can cause side-reactions. SPC is much easier to obtain and less hazardous to handle than strong H_2O_2.

This same system has been used, under different conditions, for trifluoromethylation and trifluoroacetylation of arenes.[66] Addition of SPC to a hot mixture of the arene and trifluoroacetic anhydride generates bis(trifluoroacetyl) peroxide, which rapidly decomposes to trifluoroacetyl and trifluoromethyl radicals. The ratio of trifluoromethylation to trifluoroacetylation is adjustable by varying the conditions. At 8 : 1 anhydride to H_2O_2, the results obtained with toluene are summarised in Scheme 17. It is critically important that the temperature is high enough to prevent any build-up of the peroxide concentration.

Scheme 17

Bromination can be effected with SPB and potassium bromide in an acetic acid–acetic anhydride mixture, using sodium tungstate as a catalyst for the generation of bromine from the bromide. This mixture was used for nuclear bromination of a wide range of aromatic amides.[67]

Triarylbismuth(III) compounds can be oxidised to the corresponding bismuth(V) diacetates by SPB–acetic acid.[68] Yields are good to excellent.

Finally, in another paper from Karunakaran and Muthukumaran, SPB oxidation of $[Fe(CN)_6]^{4-}$ catalysed by mercury(II) has been studied, and a mercury(II) peroxide species proposed as intermediate.[69]

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