SYNLETT Spotlight 335

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Sodium Percarbonate: A Versatile Oxidizing Reagent

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Introduction

Sodium percarbonate (SPC, Na₂CO₃·1.5H₂O) is an inorganic, inexpensive, environmentally friendly, stable, and easily handled reagent that has an excellent shelf life. The name 'sodium percarbonate' does not reflect the structure or true nature of the material. Its erroneous name is due to successive confusions in its structure.^{1,2} The structure of SPC (Figure 1) has been determined, the cohesion of the adduct being due to hydrogen bonding between carbonate ions and hydrogen peroxide molecules.^{3,4} Therefore, a more judicious appellation of SPC is 'sodium carbonate peroxyhydrate'.⁵ The structure of SPC has led it to be considered as a solid form,⁶or dry carrier of hydrogen peroxide.

SPC is relatively soluble in water (at 20 °C, 140 g/L) and the pH of 1% aqueous solution of it is ca. 10.5.⁷ The hydrogen peroxide present in SPC is spontaneously released in water. Concentrated hydrogen peroxide is not readily available and furthermore, it is more risky to handle. Consequently, the ability of SPC to release oxidative species in an organic medium has made it an useful reagent in organic synthesis.^{8–11}



Figure 1 Structure of sodium percarbonate

 $Na_2CO_3 + 1.5H_2O_2 \longrightarrow Na_2CO_3 \cdot 1.5H_2O_2$

Scheme 1 Preparation of sodium percarbonate¹²

Abstracts

(A) Oxidation of Pyridines to the Corresponding N-Oxides: A combination of Tf_2O and Na_2CO_3 ·1.5H₂O has been developed for the oxidation of highly electron-deficient pyridines.¹³ The N-oxidation reaction, utilizing in situ generated peracid, proceeds under mild conditions that allow for the presence of acid-sensitive functional groups.

(B) Asymmetric Epoxidation of α,β -Unsaturated Ketones: SPC acts as an efficient oxidant in the epoxidation of (E)- α,β -unsaturated aromatic ketones with silica-grafted poly-(L)-leucine as a chiral catalyst to yield optically active epoxy ketones in high enantio-selectivities (up to 93% ee).¹⁴



Tf₂O, SPC

MeCN. 0

(L-Leu)@AMPSi: silica-grafted poly-(L)-leucine

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0

.OH

(C) Iodination of Arenes:

An eco-friendly and easy laboratory procedures for oxidative iodination of various arenes is achieved with SPC as oxidant.¹⁵



0.

Me

R

(D) Preparation of Aromatic Carboxylic Acids:

Bjørsvik and co-workers¹⁶ oxidized methyl aryl ketones with $Na_2CO_3 \cdot 1.5H_2O$ or $NaBO_3 \cdot 4H_2O$ in the presence of a catalytic amount of nitroarenes to provide the corresponding aromatic carboxylic acids in good yields without production of any harmful side products. The method shows excellent selectivity when the model substrate (acetophenone) is oxidized.

(E) Epoxidation of α,β -Unsaturated Aldehydes: Direct asymmetric epoxidation of α,β -unsaturated aldehydes with peroxides or SPC in the presence of organocatalyst is presented. In particular, protected α,α -diphenyl-2-prolinol catalyzed the asymmetric epoxidation with excellent stereoselectivity and furnished the desired products in high efficiency with up to 96:4 dr and 98% ee.¹⁷



Highly efficient and selective oxidations of alcohols to ketones under organic-solvent-free and transition-metal-free conditions have been developed with sodium percarbonate as an oxidant. For a range of activated and non-activated alcohols the selective oxidation of secondary alcohols in the presence of primary alcoholic and other functional groups have been described.¹⁸

(G) Synthesis of Sulfoxides:

Gomez and co-workers have demonstrated that SPC can be used for the electrophilic oxidation of sulfides under solvent-free conditions. A comparative study concerning the effect of the oxidant and reaction conditions on yield and chemoselectivity (sulfoxide vs. sulfone) has been carried out.¹⁹

(H) Homocoupling:

SPC could be used both as a clean oxidant and as base in aqueous media for the Pd/Cu co-catalyzed homocoupling of terminal alkynes.²⁰

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t-BuOH (12 ml)

1,3-(O2N)2C6H4 (10 mol%)







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