SYNLETT

Spotlight 167

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

Sodium Hydrogen Sulfate: Safe and Efficient

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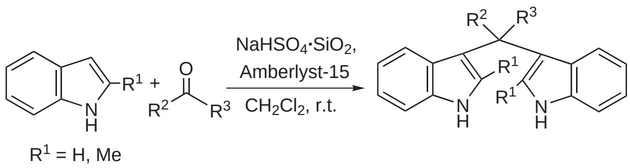
Introduction

Although $NaHSO_4$ has been known for a long time, only in recent years it emerged as an efficient catalyst in organic chemistry. The new interest in this salt is due to environmental and economical considerations that prompt urgent need to redesign important chemical processes using suitable catalysts. $NaHSO_4$ can be used alone or supported on alumina[1] or silica gel, in solvent or under solvent-free conditions. The most often used form of it is the silica gel supported form. This catalyst promotes various transformations like selective and regioselective protection and deprotection,[2–9] nitration,[10] nitrosation,[11] oxidation,[12] Beckman rearrangement,[1] synthesis of halide derivatives,[13,14] coupling of indoles,[15] and synthesis of quinazolinones.[16]

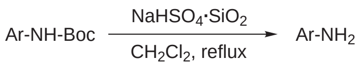
The advantages of using $NaHSO_4$ include operational simplicity, selectivity, and availability, and it is inexpensive and ecologically friendly.

Abstracts

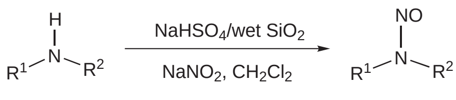
(A) Bis- and tris(1*H*-indol-3-yl)methanes are synthesized in high yields by an electrophilic substitution reaction of indoles with carbonyl compounds under mild reaction conditions using silica-supported $NaHSO_4$ and Amberlyst-15.[15]



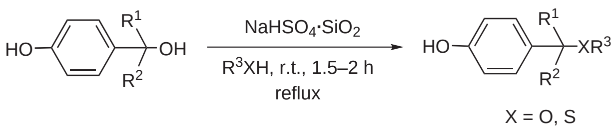
(B) Silica gel supported sodium hydrogen sulfate was found to be an efficient catalyst for the selective removal of the *N*-Boc protecting group from aromatic amines, keeping aliphatic *N*-Boc intact.[2]



(C) A combination of $NaHSO_4$ and $NaNO_2$ in the presence of wet SiO_2 was used as an effective nitrosating agent for the nitrosation of secondary amines to their corresponding nitroso derivatives under mild conditions.[11]



(D) Different *p*-hydroxybenzyl alcohols were subjected to $NaHSO_4 \cdot SiO_2$ and it was shown that this catalyst can transform *p*-hydroxybenzyl alcohols to the corresponding *p*-hydroxybenzyl ethers and thioethers efficiently and selectively.[6]



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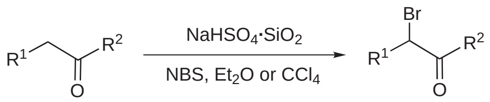
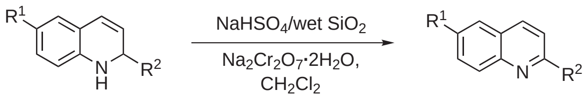
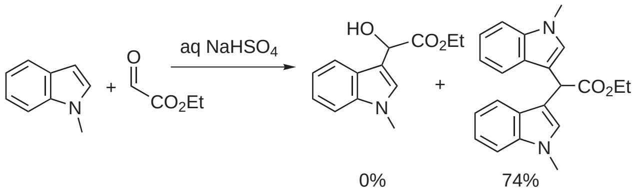
(E) Cyclic and acyclic ketones, amides, and β-keto esters were converted to their α-brominated derivatives using $NaHSO_4 \cdot SiO_2$ in the presence of NBS and with Et_2O or CCl_4 as solvent at room temperature.[13]



(F) 1,2-Dihydroquinolines were subjected to oxidation effectively and in short reaction times with $Na_2Cr_2O_7 \cdot H_2O$ and $NaHSO_4$ as catalyst. The reactions proceed under mild conditions and with dichloromethane as solvent.[12b]



(G) The reaction of ethyl glyoxylate with different heteroaromatic compounds in the presence of sodium salts was investigated. It was shown that $NaHSO_4$ is effective and affords Friedel–Crafts addition products in good yield under aqueous conditions.[17]



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