

# SYNLETT Spotlight 349

## Sodium Bromate: An Eco-Friendly Brominating and Oxidizing Reagent

Compiled by Jie Lu



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

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### Introduction

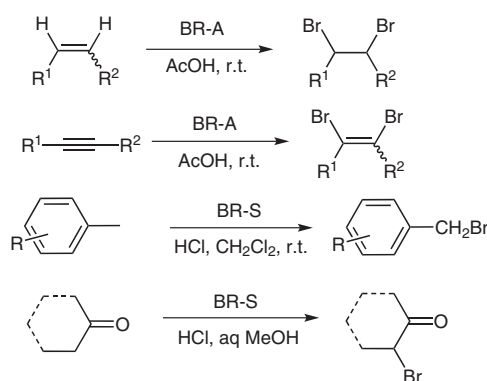
Sodium bromate is commercially available as an inexpensive stable white crystal, and has been extensively used in organic synthesis as an eco-friendly brominating and oxidizing reagent. It decomposes at 381 °C with liberation of oxygen. It can oxidize primary alcohols to aldehydes, secondary alcohols to ketones, sulfides to sulfoxides, hydroquinones and polyaromatics to quinones, thiols to disulfides, iodobenzenes to iodoxybenzenes, and  $\omega,\omega$ -diols to dicarboxylic acids or lactones. Under different sets of conditions, the oxidation can result in the formation of esters and carboxylic acids.<sup>1</sup> It has been used for oxidative

cleavages of alkyl, trimethylsilyl, *t*-butyldimethylsilyl, tetrahydropyranyl ethers, and ethylene acetals to the corresponding carbonyl compounds.<sup>2,3</sup> The transformations of benzylidene acetals to hydroxy esters with  $\text{NaBrO}_3 \cdot \text{Na}_2\text{S}_2\text{O}_4$  in EtOAc–H<sub>2</sub>O biphasic medium are readily accomplished.<sup>4,5</sup> Even more interesting is the finding that the reaction of cyclic ethers with sodium bromate in the presence of catalytic amounts of hydrobromic acid gave lactones.<sup>6</sup> Sodium bromate can also serve as an effective bromohydroxylation reagent for alkenes, alkynes, and allylic alcohols.<sup>7</sup> It has also been reported to be a powerful brominating agent for aromatic compounds including phenols, anilines, aromatic ethers, and benzenes.<sup>8,9</sup>

### Abstracts

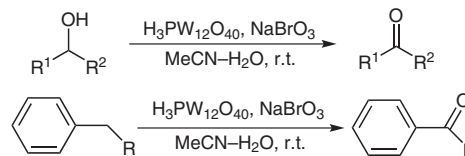
#### (A) Regio- and Stereoselective Bromination of Alkenes, Alkynes, Toluenes, and Ketones:

An efficient NaBr/NaBrO<sub>3</sub> system for the bromination of alkenes, alkynes, toluenes, and ketones has been developed by Adimurthy and co-workers.<sup>10</sup> Treatment of several structurally diverse alkenes and alkynes with NaBr/NaBrO<sub>3</sub> (5:1, BR-A) lead to the corresponding dibromides. On the other hand, the regioselective bromine substitution at the  $\alpha$ -carbon of ketones and at the benzylic position of toluene derivatives can be accomplished with treatment with NaBr/NaBrO<sub>3</sub> (2:1, BR-S) in aqueous acidic methanol or dichloromethane.



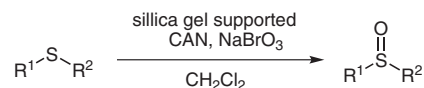
#### (B) Oxidation of Alkyl Arenes and Alcohols to the Corresponding Carbonyl Compounds:

The oxidation of primary and secondary alcohols with NaBrO<sub>3</sub> and tungstophosphoric acid lead to aldehydes and ketones, respectively. In a similar manner, alkyl benzenes are regioselectively oxidized at the  $\alpha$ -position to afford the corresponding ketones.<sup>11</sup> The oxidation of alcohols and alkyl benzenes to carbonyl compounds can also be performed by treatment with NaBrO<sub>3</sub> in ionic liquids.<sup>12</sup>



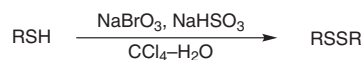
## (C) Oxidation of Sulfides to Sulfoxides:

The oxidation of sulfides with  $\text{NaBrO}_3$  in the presence of a catalytic amount of ceric ammonium nitrate (CAN) supported on silica lead to excellent yields of the corresponding sulfoxides with no overoxidation to sulfones.<sup>13</sup> The oxidations of sulfides to sulfoxides can also be accomplished using an immobilized vanadyl, cobalt or nickel alkyl phosphonates.<sup>14</sup>

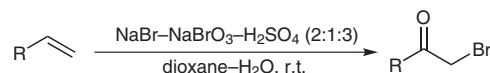


## (D) Synthesis of Disulfides:

Khan and co-workers have reported that various aliphatic and functionalized aromatic thiols can be converted into the corresponding disulfides using  $\text{NaBrO}_3$  in a two-phase system of carbon tetrachloride and water in the presence of  $\text{NaHSO}_3$ .<sup>15</sup> Furthermore, amino group, aliphatic alcohols and phenols were not affected under the same oxidative conditions.

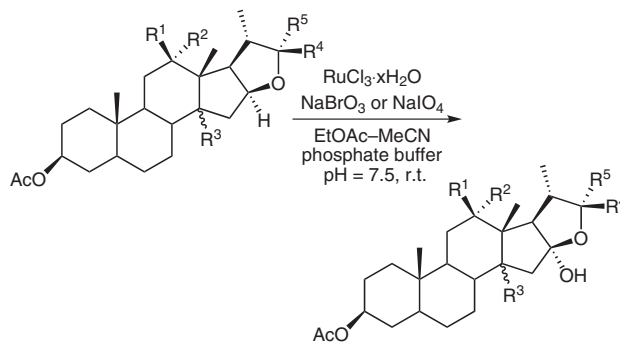
(E) One-Pot Synthesis of  $\alpha$ -Bromo Ketones:

Patil et al. reported that  $\text{NaBr}/\text{NaBrO}_3$  can serve as an efficient and green brominating agent for the synthesis of  $\alpha$ -bromo ketones by direct oxybromination of olefins.<sup>16</sup>

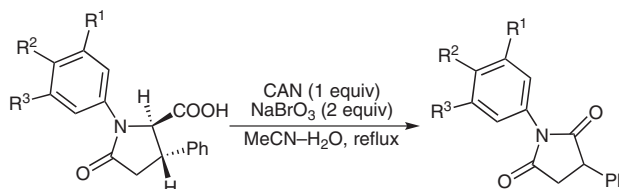


## (F) Carbon-Hydrogen Oxyfunctionalization of Cyclic Steroidal Ethers:

Lee and co-workers reported a new, mild protocol for site-specific carbon-hydrogen oxyfunctionalization of cyclic steroidal ethers using  $\text{NaBrO}_3$  or  $\text{NaIO}_4$  as terminal oxidants in biphasic  $\text{EtOAc}/\text{MeCN}/\text{phosphate buffer}$  (pH 7.5) in the presence of catalytic amounts of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ .<sup>17</sup>

(G) Synthesis of *N*-Phenylsuccinimides:

A convenient and practical method for the synthesis of *N*-phenylsuccinimides by decarboxylative oxidation of *N*-aryl- $\gamma$ -lactam-2-carboxylic acids with  $\text{NaBrO}_3$  in combination with ceric ammonium nitrate (CAN) has been developed.<sup>18</sup> The reactions were performed in  $\text{MeCN-H}_2\text{O}$  at 80 °C to furnish exclusively the 1,3-diaryl succinimides in high yields.



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