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Spotlight 349Sodium 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 ω,ω -diols to dicarboxylic acids or lactones. Under different sets of conditions, the oxidation can result in the formation of esters and carboxylic acids.¹ It has been used for oxidative

cleavages of alkyl, trimethylsilyl, *t*-butyldimethylsilyl, tetrahydropyranyl ethers, and ethylene acetals to the corresponding carbonyl compounds.^{2,3} The transformations of benzyldiene acetals to hydroxy esters with $\text{NaBrO}_3 \cdot \text{Na}_2\text{S}_2\text{O}_4$ in $\text{EtOAc-H}_2\text{O}$ biphasic medium are readily accomplished.^{4,5} 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.⁶ Sodium bromate can also serve as an effective bromohydroxylation reagent for alkenes, alkynes, and allylic alcohols.⁷ It has also been reported to be a powerful brominating agent for aromatic compounds including phenols, anilines, aromatic ethers, and benzenes.^{8,9}

Abstracts

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

An efficient $\text{NaBr}/\text{NaBrO}_3$ system for the bromination of alkenes, alkynes, toluenes, and ketones has been developed by Adimurthy and co-workers.¹⁰ Treatment of several structurally diverse alkenes and alkynes with $\text{NaBr}/\text{NaBrO}_3$ (5:1, BR-A) lead to the corresponding dibromides. On the other hand, the regioselective bromine substitution at the α -carbon of ketones and at the benzylic position of toluene derivatives can be accomplished with treatment with $\text{NaBr}/\text{NaBrO}_3$ (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_3 and tungstophosphoric acid lead to aldehydes and ketones, respectively. In a similar manner, alkyl benzenes are regioselectively oxidized at the α -position to afford the corresponding ketones.¹¹ The oxidation of alcohols and alkyl benzenes to carbonyl compounds can also be performed by treatment with NaBrO_3 in ionic liquids.¹²

(C) Oxidation of Sulfides to Sulfoxides:

The oxidation of sulfides with 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.¹³ The oxidations of sulfides to sulfoxides can also be accomplished using an immobilized vanadyl, cobalt or nickel alkyl phosphonates.¹⁴

(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 NaBrO_3 in a two-phase system of carbon tetrachloride and water in the presence of NaHSO_3 .¹⁵ Furthermore, amino group, aliphatic alcohols and phenols were not affected under the same oxidative conditions.

(E) One-Pot Synthesis of α -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 α -bromo ketones by direct oxybromination of olefins.¹⁶

(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 NaBrO_3 or NaIO_4 as terminal oxidants in biphasic $\text{EtOAc}/\text{MeCN}/\text{phosphate buffer}$ (pH 7.5) in the presence of catalytic amounts of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$.¹⁷

(G) Synthesis of *N*-Phenylsuccinimides:

A convenient and practical method for the synthesis of *N*-phenylsuccinimides by decarboxylative oxidation of *N*-aryl- γ -lactam-2-carboxylic acids with NaBrO_3 in combination with ceric ammonium nitrate (CAN) has been developed.¹⁸ 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.

References

- (1) Krapcho, A. P. *Org. Prep. Proced. Int.* **2006**, 38, 177.
- (2) Olah, G. A.; Gupta, B. G. B.; Fung, A. P. *Synthesis* **1980**, 897.
- (3) Mohammadpoor-Baltork, I.; Nourozi, A. R. *Synthesis* **1999**, 487.
- (4) Srimurugan, S.; Suresh, P.; Viswanathan, B.; Varadarajan, T. K. *Synth. Commun.* **2007**, 37, 2483.
- (5) Bishop, M.; Cmrecki, V.; Ophoven, V.; Pietruszka, J. *Synthesis* **2008**, 2488.
- (6) Kajigaeshi, S.; Nakagawa, T.; Nagasaki, N.; Yamasaki, H.; Fujisaki, S. *Bull. Chem. Soc. Jpn.* **1986**, 59, 747.
- (7) (a) Masuda, H.; Takase, K.; Nishio, M.; Hasegawa, A.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1994**, 59, 5550.
(b) Agrawal, M. K.; Adimurthy, S.; Ganguly, B.; Ghosh, P. K. *Tetrahedron* **2009**, 65, 2791.
- (8) Groweiss, A. *Org. Process Res. Dev.* **2000**, 4, 30.
- (9) Adimurthy, S.; Ramachandraiah, G.; Bedekar, A. V.; Ghosh, S.; Ranu, B. C.; Ghosh, P. K. *Green Chem.* **2006**, 8, 916.
- (10) Adimurthy, S.; Ghosh, S.; Patoliya, P. U.; Ramachandraiah, G.; Agrawal, M.; Gandhi, M. R.; Upadhyay, S. C.; Ghosh, P. K.; Ranu, B. C. *Green Chem.* **2008**, 10, 232.
- (11) Shaabani, A.; Behnam, M.; Rezayan, A. H. *Catal. Commun.* **2009**, 10, 1074.
- (12) Shaabani, A.; Farhangi, E.; Rahmati, A. *Monatsh. Chem.* **2008**, 139, 905.
- (13) Ali, M. H.; Kriedelbaugh, D.; Wenciewicz, T. *Synthesis* **2007**, 3507.
- (14) Al-Hashimi, M.; Fisset, E.; Sullivan, A. C.; Wilson, J. R. H. *Tetrahedron Lett.* **2006**, 47, 8017.
- (15) Khan, K. M.; Ali, M.; Taha, M.; Perveen, S.; Choudhary, M. I.; Voelter, W. *Lett. Org. Chem.* **2008**, 5, 432.
- (16) Patil, R. D.; Joshi, G.; Adimurthy, S.; Ranu, B. C. *Tetrahedron Lett.* **2009**, 50, 2529.
- (17) Lee, J. S.; Cao, H.; Fuchs, P. L. *J. Org. Chem.* **2007**, 72, 5820.
- (18) Barman, G.; Roy, M.; Ray, J. K. *Tetrahedron Lett.* **2008**, 49, 1405.