



# Green, mild and efficient bromination of aromatic compounds by HBr promoted by *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane in water as a solvent

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## Abstract

A combination of HBr and *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane as a new and powerful oxidant was found effective for facile bromination of different aromatic compounds at room temperature in water as a green solvent. Mild reaction conditions, high selectivity and yield, high reaction rate and non-toxicity are some of the major advantages of this synthetic protocol.

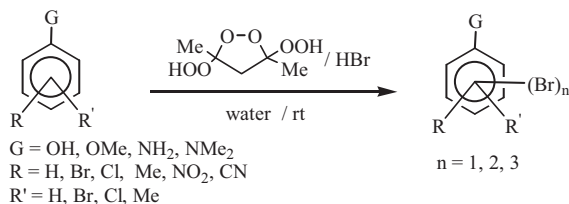
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**Keywords:** *Trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane; HBr; Bromination; Anilines; Phenoles

The bromination of aromatic substrates is very important and is an interesting deal in organic chemistry because of the commercial importance of brominated compounds in synthesis of natural products and biological active compounds such as potent antitumor, antibacterial, antifungal, antiviral and anti oxidizing agents [1]. Unfortunately, reported conventional aromatic bromination methods that have used toxic elemental bromine or hazardous acidic reagents, generate toxic, corrosive and environmental pollutant wastes [2]. Examples of these methods include: Br<sub>2</sub>–Lewis acids [3], NBS–H<sub>2</sub>SO<sub>4</sub>–CF<sub>3</sub>CO<sub>2</sub>H [4], NBS–PTSA [5], NBS–NaOH [6], NBS–SiO<sub>2</sub> [7], Br<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> [8], Br<sub>2</sub>–Zeolite [9], NBS–Amberlyst [10], NBS–HZSM-5 [11], Clayzib [12], *tert*-BUOOH- or H<sub>2</sub>O<sub>2</sub>–HBr [13], HBr–DMSO [14], Br<sub>2</sub>–SO<sub>2</sub>Cl<sub>2</sub> [15], *N,N,N,N*-tetrabromobenzen-1,3-disulfonylamide [16], hexamethylenetetramin–2Br<sub>2</sub> [17], KBr–benzyltriphenylphosphonium peroxymonosulfate [18], NBS–Al<sub>2</sub>O<sub>3</sub> [19], NBS–NH<sub>4</sub>OAc [20], NBS–TEAB [21], NBS–Pd(OAc)<sub>2</sub> [22], NBS–DMF (or THF) [23], CuBr<sub>2</sub> [24], alkylpyridinium tribromide [25], tribromoiso-cyanouric acid [26], bromodichloroisocyanuric acid [27], polymer-supported organotin reagents [28], NH<sub>4</sub>VO<sub>3</sub>–H<sub>2</sub>O<sub>2</sub>–HBr [29], [Bmim]Br<sub>3</sub> [30], NBS–CCl<sub>4</sub> [37], poly(diallyldimethylammonium tribromide [38], *etc.* Replacement of such reagents with non-toxic, inexpensive, available and more selective reagents is very interesting and still represents an important goal in the context of clean synthesis. Recently, synthesis of *gem*-dihydroperoxides and their applications as affective oxidants have been reported [31]. Newly, we have reported the synthesis of *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane and its applications as new, solid and affective oxidant [32]. In this work,

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Scheme 1.

we have used *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane for *in situ* generation of Br<sup>+</sup> from HBr and we wish to report the bromination of aromatic substrates by this system in green and mild condition with excellent yields (Scheme 1). In order to establish the conditions of the titled reactions, we initially examined the bromination of phenol (1 mmol) as test compound. The effects of solvent and oxidant were studied using different solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>, MeCN, and water under various amounts of oxidant. It was noticed that, the best results for monobromination (93%, Table 2, entry 1), dibromination (93%, Table 2, entry 2) and tribromination (91%, Table 2, entry 3) using respectively 1.1, 2.2 and 3.5 mmol of HBr were obtained when the reactions were conducted under stirring at room temperature in water as the solvent of choice. To develop the scope of these reactions, several other aromatic substrates were subjected to bromination under the optimized conditions. The experimental results are summarized in Table 2. As shown in Table 2, the phenols and also the anilines with both electron-withdrawing groups and electron-releasing groups are brominated by this method. As is anticipated for electrophilic substitutions, the electron-withdrawing groups decrease the rate of reaction (7, 8, 9, 16, 17, 22, and 23 entries) and the electron-releasing groups increase the rate of reaction (10, 13, 14, 15, and 18 entries). Also, three-bromination and di-bromination is more slow than mono-bromination because of steric hindrance of Br atoms.

*Trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane is a solid, powerful, non-toxic, inexpensive and effective oxidant that is synthesized easily [32] and seems that it can eliminate the defects of hydrogen peroxides (such as problems of weighing, weak power in organic liquids, having the water, needing catalyst, etc.). So, we have used it for *in situ* generation of Br<sup>+</sup> from HBr as an effective electrophilic species. Then, this generated Br<sup>+</sup> attack to aromatic ring and finally, after losing H<sup>+</sup>, the aromaticity of ring will obtain again (Scheme 2). The results of this methodology are compared with other brominating methods in Table 1. Clearly, the reaction times and yields by this method are notable in compare with other bromination methods.

In summary, *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane has been conveniently used as an efficient and high potent oxidant for *in situ* generation of Br<sup>+</sup> ion in reaction with HBr. This ion can subsequently act as reactive electrophiles towards the aromatic substrates to afford the corresponding brominated products in quantitative yields. The reactions proceed under mild conditions at room temperature with a simple work up procedure. This protocol is green and considered as environmentally benign since no toxic residues or corrosive acids are introduced to the environment.

Chemicals used in this work were purchased from Fluka and Merck chemical companies and used without purification. IR spectra were recorded on a PerkinElmer GX FT IR spectrometer from KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR

Table 1  
 Reaction times and yield for previously published methods.

Substrate	Product	Condition	Time (h)	Yield (%)	Ref.
C <sub>6</sub> H <sub>5</sub> OH	4-BrC <sub>6</sub> H <sub>4</sub> OH	This method	0.4	93	–
C <sub>6</sub> H <sub>5</sub> OH	4-BrC <sub>6</sub> H <sub>4</sub> OH	Hexamethylenetetramine–bromine, –15 °C	1.5	45	[17]
C <sub>6</sub> H <sub>5</sub> OH	4-BrC <sub>6</sub> H <sub>4</sub> OH	PhCH <sub>2</sub> Ph <sub>3</sub> PFSO <sub>3</sub> /KBr	5	88	[18]
C <sub>6</sub> H <sub>5</sub> OH	4-BrC <sub>6</sub> H <sub>4</sub> OH	ZrBr <sub>4</sub> /diazene mixture, 0 °C, argon	0.67	82	[33]
C <sub>6</sub> H <sub>5</sub> OH	4-BrC <sub>6</sub> H <sub>4</sub> OH	Potassium bromide and hydrogen peroxide over zeolites	5	58	[34]
C <sub>6</sub> H <sub>5</sub> OH	4-BrC <sub>6</sub> H <sub>4</sub> OH	Heteropoly acid cesium salt/cetyltrimethylammonium bromide/Br <sub>2</sub>	15+ Im	94	[35]
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	4-BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	This method	0.2	84	–
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	4-BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	Tetrabutylammonium Bromide Promoted by V <sub>2</sub> O <sub>5</sub> –H <sub>2</sub> O <sub>2</sub>	0.5	82	[2]
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	4-BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	Hexamethylenetetramine–bromine, –15 °C	0.75	85	[17]
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	4-BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	ZrBr <sub>4</sub> /diazene mixture, 0 °C, argon	6	66	[33]
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	4-BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	Tetrabutylammonium peroxydisulfate	1	86	[36]

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