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Graphical Abstract

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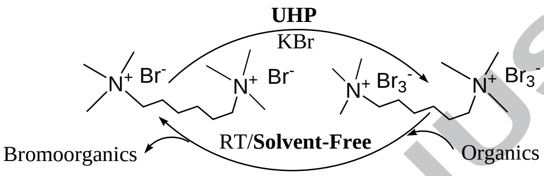

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Hexamethonium bis(tribromide) (HMBTB) a recyclable and high bromine containing reagent

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ABSTRACT

A recyclable and high bromine containing di-(tribromide) reagent, hexamethonium bis(tribromide) (HMBTB) has been synthesized and utilized for the bromination of various organic substrates. The spent reagent hexamethonium bromide (HMB) can be effectively recycled by regenerating and reusing it without significant loss of activity. The crystalline and stable bis(tribromide) is an effective storehouse of very high percentage of active bromine requiring just half an equivalent of it for complete bromination. Both the Br_3^- moieties in HMBTB are nearly linear with Br-Br-Br angle of 179.55°.

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1. Introduction

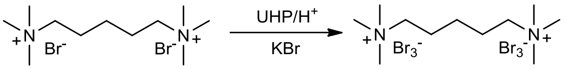
Bromination is a an important synthetic process as bromo-organics are often used as intermediates in the synthesis of pharmaceuticals, agrochemicals and other speciality chemicals.[1] Numerous industrially important products such as pesticides, insecticides, herbicides and fire retardants contain bromo-functionality.[2] These bromo-organics are precursors to C–C bond C–X (X= heteroatom) bond forming processes.[3,4] The use of liquid bromine in industry as well as in academia is still a common practice, in spite of its associated hazards. Furthermore, bromination of an aromatic substrate using bromine involving an electrophilic substitution results in the formation of HBr as by-product thereby reduces the atom efficiency to 50%. However, besides liquid bromine, several other safer and user-friendly brominating agents such as tribromide,[5-11] Importantly, a few ditribromides and ionic liquid tribromides[12-16] have also made a prominent mark as brominating agents. Most of the tribromides mentioned above although are safe, user-friendly, stable, easy to store and transport but preparation of some of these reagents invariably involve direct or indirect use of toxic liquid bromine.

Ditribromides are considered to be superior to quaternary ammonium tribromides (QATBs) mainly due to higher content of active of bromine and less phase-transfer property. Moreover, most of the QATBs contain expensive organic ammonium cation and use only 1/3 of its total bromine for an aromatic electrophilic substitution type reaction and 2/3 for addition of bromine across C–C multiple bonds. Some of QATBs posses phase transfer properties due to which organic ammonium cation become soluble in the solvent used for the extraction of brominated products, causing considerable difficulty in work-up and purification process. Therefore such QATBs are not preferable as brominating agent particularly in large scale reaction. There are some issues regarding stability and selectivity of a few organic ammonium tribromides such as pyridinium hydrotribromide,[17] N-methylpyrollidi-2-one hydrotribromide,[18] in spite of their versatility as reagent for other reactions. Moreover, recovery and recyclability of QATBs have not been explored adequately. We have already reported[12] that ditribromides have the features that can overcome most of these aforementioned drawbacks of QATBs.

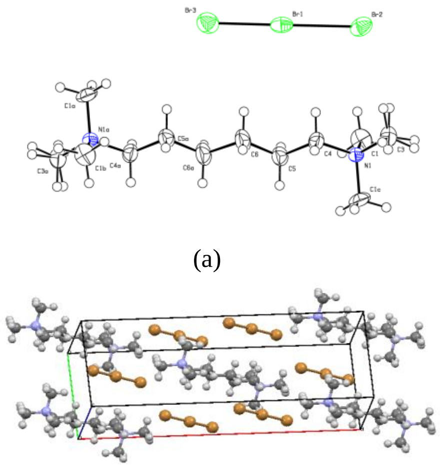
Development of efficient and environmentally benign processes with simple work-up coupled with high purity and high yield of the products is currently receiving a lot of interest. In this context, ditribromides with high percentage of active bromine, play an important role for obtaining bromo-derivatives in hazard-free, waste-free and solvent-free manner. As mentioned previously ditribromides with high bromine content and recyclability, are gaining popularity over monotribromides, particularly from green chemistry perspective. In continuation our interest on synthesis and application of organic ammonium ditribromides,[12,14,19] we wish to report herein, an environmentally favourable synthesis of a novel ditribromide and its use as recyclable and efficient brominating reagent.

2. Results and discussion

The procedure for synthesis of HMBTB is rather simple. Hexamethonium bromide (HMB) (1 equiv), potassium bromide (4 equiv) and urea-hydrogen peroxide (UHP) (4 equiv) along with 4N H_2SO_4 (4 equiv) were mixed in a beaker. After continuous stirring for 5 min, an orange-yellow product was obtained indicating the formation of a ditribromide (Scheme 1). The product was separated by filtration from other components after washing thoroughly with water (2 x 10 mL). The product so obtained was recrystallized from acetonitrile. The crystallized product has shelf life up to six months. The role of UHP here was to oxidize Br^- to Br_3^- in the presence of H_2SO_4. The UHP a non-toxic solid with relatively high proportion of hydrogen peroxide in urea adduct (36.2%). Its safe handling, smooth decomposition into environmentally friendly substances such water and urea, ensures its place among the top ecofriendly oxidants. The hydrogen peroxide present in UHP, safely oxidizes Br^- to Br_3^- without the need of any transition metal activator, making it an environmentally safe metal-free process. Interestingly, UHP sets free H_2O_2 for oxidation of Br^- to Br_3^- leaving behind the urea. The left behind urea upon treatment with 30% hydrogen peroxide at 60°C for a few minutes regenerates urea hydrogen peroxide. Thus choice of UHP for the preparation tribromides is favourable from green chemistry perspective. This novel ditribromide was characterized by single crystal XRD technique, ^1H NMR, FTIR and UV-visible spectroscopy and CHN analysis. The crystal structure reveals that both the Br^- ions of hexamethonium bromide (HMB) are converted to Br_3^- in HMBTB, thereby confirming the formation of ditribromide (Figure 1a and 1b). The Br_3^- moiety is linear with Br-Br-Br bond angle of 179.55° (Figure 1a). Other analytical data are also evidential in support of the formation Br_3^- (See Supporting information).



Scheme 1. Formation of HMBTB from hexamethonium bromide



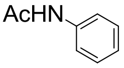
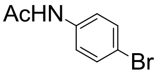
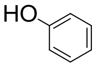
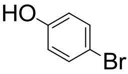
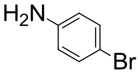
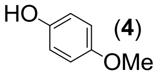
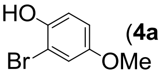
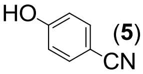
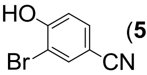
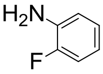
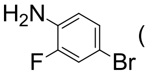
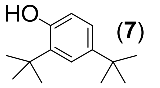
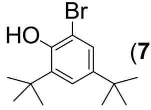
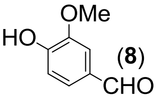
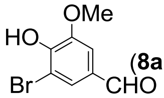
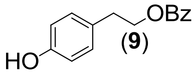
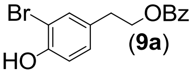
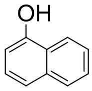
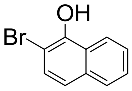
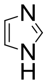
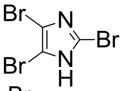
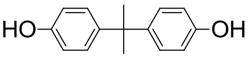
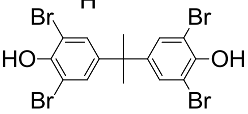
(a)

(b)

Figure 1. (a) ORTEP view of HMBTB (b) crystal packing of HMBTB showing formation of di(tribromide)

Inspired by our earlier success with ditribromides as brominating reagent,[12,14,19] we have endeavoured into synthesis of this novel ditribromide, hexamethonium bis(tribromide), which has nearly same bromine content but better efficiency and stability. This novel reagent has variable solubility in different polar protic and aprotic solvents but insoluble in non-polar aprotic solvent such as dichloromethane, toluene, petroleum ether etc. Importantly, the precursor of the reagent *i.e.* HMB (hexamethonium bromide) is highly soluble in water. This property of the reagent may help in clean and easy separation of brominated products as well as efficient recovery of the HMB, which may be advantageous over other ammonium tribromides. To explore the versatility of this reagent, large variety of organic substrates were chosen for bromination (Table 1 and 2). Customarily bromination of an organic substrate by tribromides is carried out with 1:1 molar ratio of substrate to reagent. We have chosen acetanilide (**1**) as the model substrate to test bromination efficiency of HMBTB with a substrate to reagent ration of 1:0.5 in acetonitrile. The reaction appeared to be complete within 30 min as observed from TLC with nearly quantitative precipitation of solid spent reagent HMB. While the HMB was filtered and recovered for further use, the CH_3CN solution was concentrated to obtain *p*-bromoacetanilide in 95% yield. Thus bromination of *p*-acetanilide (**1a**) using HMBTB shows that the reagent is worthy of not only a very good bromine carrier but also able to transfer it selectively and efficiently to the organic substrate (Table 1). This procedure was successfully applied to number of other substrates. Even though acetonitrile is an ecofriendly solvent but our objective was to explore bromination in solvent-free condition. In the solvent-free version, acetanilide was treated with HMBTB in a molar ratio of 1:0.5 of substrate to reagent in a mortar and pestle and the mixture was agitated form time to time for a period of 20 min. The progress of the reaction as indicated by GC showed more than 99% conversion to *p*-bromoacetanilide after 20 min. The mixture was treated with water (5 mL) and allowed to pass through a filter paper. The residue containing *p*-bromoacetanilide was further washed with water (2 x 5 mL) to afford the product in 95% yield. Bromination of phenol (**2**) and aniline (**3**) is important as their bromo derivatives are known to be intermediates to a variety of synthetic transformations. Thus realizing the importance of bromo derivatives of these substrates, we extended the solvent-free methodology of bromination by HMBTB for these substrates as well. As expected, *p*-bromophenol (**2a**) and *p*-bromoaniline (**3a**) were obtained regioselectively in very high yield (Table 1). The reagent transfers bromine only in contact with the substrate and with controlled stoichiometry, formation of polybrominated products can be completely arrested. The versatility of the reagent can also be clearly brought out with exclusive regioselective bromination of majority of substrates (Table 1). It can be seen for substrates **4-6** that regioselectivity of this reagent is emphatic, when both *o, p-* directing groups are present in the aromatic ring. Substrates containing various combinations of functional groups were exclusively and selectively monobrominated (**7-8**) (Table 1). Phenolic substrate containing benzoyl group (**9**) withstood the described reaction conditions to give corresponding *o*-bromo product (**9a**). The fused ring phenolic compound α-naphthol (**10**) afforded the expected 2-bromo-α-naphthol (**10a**). Heterocyclic compounds such as imidazole (**11**) which is sensitive to usual bromination, can be brominated by this reagent to 2,4,5-tribromoimidazole (**11a**) in reasonably high yield using 1.5 equiv of the reagent (Table 1). 2,4,5-Tribromoimidazole is believed to be capable of catalytically reactivating phosphorylated acetocholinestearase.[20] In another interesting reaction bisphenol-A (**12**) was brominated to tetrabromobisphenol-A (**12a**) by using 2 equiv of the reagent (Table 1). It may be cited here that tetrabromobisphenol-A is well known fire retardant.[21] The reagent is equally efficient for bromination of substrates bearing several other functionalities such as ethylenic and acetylinic, carbonyl as well as active methylene of 1,3-diketone and β-ketoester. For example substrates **13-15** (Table 2) were all brominated to their corresponding *trans*-dibromo compounds with 0.5 equivalent of the reagent. The methodology has also been proved to be effective for carrying out bromination of α,β-unsaturated ketones such as 4-phenylbut-3-en-2-one (**16**) to its corresponding *erythro*-dibromo product (**16a**). Bromination of cinnamaldehyde diacylate (**17**) afforded corresponding *erythro*-dibromo product (**17a**) in excellent yield without affecting the acylal functionality under present reaction conditions (Table 2). The present reagent is capable of chemoseletively brominate only one double bond in a substrate containing two symmetrical double bonds as demonstrated for dibenzylidene (**18**) (Table 2).

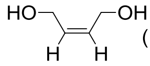
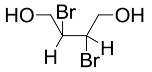
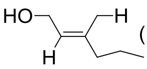
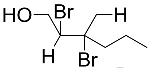
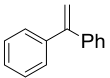
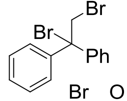
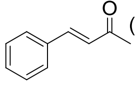
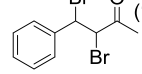
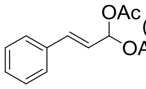
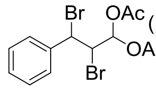
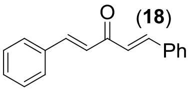
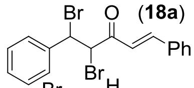
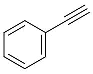
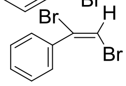
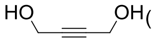
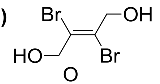
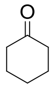
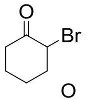
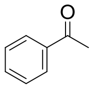
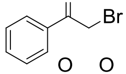
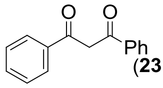
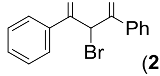
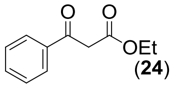
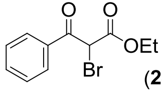
Table 1. Bromination[a] of organic substrates with HMBTB under solvent-free condition

Substrate	Product	Time (min)	Yield^{b,c}
 (**1**)	 (**1a**)	20	95
 (**2**)	 (**2a**)	30	85
 (**3**)	 (**3a**)	30	85
 (**4**)	 (**4a**)	20	90
 (**5**)	 (**5a**)	20	88
 (**6**)	 (**6a**)	20	90
 (**7**)	 (**7a**)	20	92
 (**8**)	 (**8a**)	20	90
 (**9**)	 (**9a**)	20	88
 (**10**)	 (**10a**)	20	88
 (**11**)	 (**11a**)	60	70
 (**12**)	 (**12a**)	60	60

[a]Reactions were monitored by TLC. [b]Isolated yields. [c]Products were characterized by comparison of their spectral data with those of authentic samples (please see ESI)

Acetylinic substrates (**19**) and (**20**) could also be brominated with this reagent in very good yields Successful α-bromination of ketones such as cyclohexanone (**21**) and acetophenone (**22**) has been achieved as well (Table 2). Finally we have also studied monobromination of active methylene compounds. Whereas such bromination with conventional reagents is difficult[22] the reaction could be achieved in good yield with present regent. Bromination of 1,3-diketone such as 1,3-diphenylpropane-1,3-dione (**23**) as well as ethyl-3-oxo-3-phenylpropionate (**24**) gave exclusively α-monobrominated product (**23a** and **24a**) with 0.5 equiv of the reagent (Table 2).

Table 2. Bromination[a] of organic substrates with HMBTB under solvent-free condition

Substrate		Product		Time(min)	Yield[b,c]
	(**13**)		(**13a**)	20	90
	(**14**)		(**14a**)	30	90
	(**15**)		(**15a**)	20	88
	(**16**)		(**16a**)	20	90
	(**17**)		(**17a**)	20	91
	(**18**)		(**18a**)	20	90
	(**19**)		(**19**)	30	85
	(**20**)		(**20a**)	20	88
	(**21**)		(**21a**)	60	85
	(**22**)		(**22a**)	60	85
	(**23**)		(**23a**)	20	19
	(**24**)		(**24a**)	40	85

[a]Reactions were monitored by TLC. [b]Isolated yields. [c]Products were characterized by comparison of their spectral data with those of authentic samples (please see ESI)

A comparative study of this reagent with three other reported ditribromides (Figure 2), *viz.*, 1,2-dipyridiniumditribromide-ethane (DPTBE) (**II**), 1,10-(ethane-1,2-diyl)phenanthrolinediium bistribromide (EPDBT) (**III**), ethylenebis(*N*-methylimidazolium) ditribromide (EBMIDTB) (**IV**) has been made by carrying out bromination of phenol, aniline, acetanilide and *p*-methoxyphenol for amount of time mentioned in Table 1. The results are summarized in Table 3. The results clearly indicate that although active bromine (47%) content of HMBTB (**I**) is comparable to these ditribromides, DPTBE (**II**), (48%), EPDBT (**III**), (46.5%) and EBMIDTB (**IV**), (47.6%) but it certainly proves to be superior in terms of yield and reaction times under similar reaction conditions (Table 3).

Another intriguing feature of this reagent is its easy recoverability and reusability. The regeneration of this reagent is simple as its precursor spent reagent HMB is highly water soluble. For reactions that involve transfer of one bromine atom to the substrate such as monobromination of aromatic ring, 1,3-diketones etc., the aqueous solution containing the precursor (HMB) and 2 equiv of leftover bromide, needs to be treated with 1.2 equiv of KBr and 1.1 equiv of UHP under mild acidic condition to regenerate the reagent in quantitative yield. For reactions involving addition of bromine across a double bond, 2 equiv of KBr and 2 equiv of UHP are required. The recovered reagent shows same efficiency as that of the parent reagent.

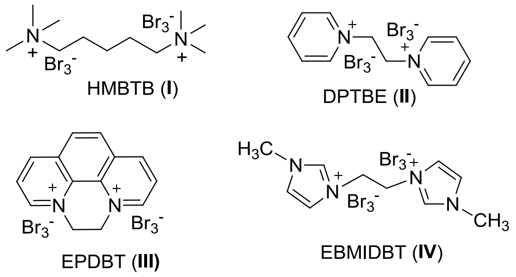


Figure 2. Various ditribromide reagents

Table 3. Comparison of HMBTB with other ditribromides in regioselective bromination of phenol (**2**), aniline (**3**), acetanilide (**1**), and *p*-methoxyphenol (**4**)

Reagent	% of product (isolated yields/ GC yields)			
	Phenol (**2**)	Aniline (**3**)	Acetanilide (**1**)	*p*-Methoxy phenol (**4**)
HMBTB (I)	85/90	85/91	95/99	95/99
DPTBE (II)	85/89	85/90	95/99	90/96
EPDBT (III)	81/85	80/86	88/95	82/88
EBMIDTB (IV)	80/85	81/86	88/96	85/90

A comparative study on recoverability and recyclability of HMBTB has been carried out with aforementioned ditribromides. The spent reagents recoverability for HMBTB (I), DPTBE (II), EPDBT (III) and EBMIDTB (IV) are respectively, 97%, 93%, 95% and 91%. While the overall recoverability of their corresponding tribromides are 92%, 88%, 85% and 85% respectively. These results suggest HMBTB (I) can be overall recovered better compared to other ditribromides.

To conclude, an ecofriendly synthesis of novel ditribromide *viz.*, hexamethonium bis(tribromide) from hexamethonium bromide is reported. Urea-hydrogen peroxide was used to oxidize bromide to tribromide. The reagent contains nearly 47% active bromine per molecule which is one of the highest among reported organic ammonium tribromides. The reagent makes nearly 100% efficient delivery of bromine to organic substrate making the bromination reaction highly atom economic. The other features of bromination reactions involving the present reagent that are important from Green chemistry perspective are solvent-free conditions, high yield and high selectivity of products and ability to react towards wide range of substrates. These advantages coupled with ease of recovery and reuse of the HMBTB, make it a reagent of choice for bromination reactions. All in all, the reagent is believed to complement other green ditribromides, particularly DPTBE, in bromination of organic substrates.

3. Experimental

Preparation of hexamethonium bis(tribromide) (HMBTB): Hexamethonium bromide (HMB) (100 mmol, 36.2g) and KBr (400 mmol, 48.0g), were dissolved to 100 mL of 4N sulfuric acid. To this solution was added urea-hydrogen peroxide (UHP) (400 mmol, 37.0g) over a period of 10 min at room temperature. The solution was stirred magnetically for *ca*. 15 min to afford an orange yellow product. The stirring was continued for another 15 min to ensure complete conversion of HMB to HMBTB. The orange-yellow precipitate was filtered, dried in vacuum desiccator and recrystallized from CH_3CN to yield 66.5g (96%) of hexamethonium bis(tribromide). Mp 118-120 °C. UV (CH_3CN) 267 nm. FT-IR (KBr, cm^{-1}): 650,491, 448, 262, 243, 132 121. ^{1}H NMR (d$_6$-DMSO) δ: 3.7 (m, 18H), 3.1 (m, 4H), 2.6 (m, 4H), 2.1 (m, 4H). Elemental Anal. Calcd for $C_{12}H_{30}N_2Br_6$ (Mol Wt. 682.19): C 21.15, H 4.34, N 4.11, Br 70.31. Found C 21.17, H 4.37, N 4.13, Br 70.33.

Bromination of phenol (2) to *p*-bromophenol (2a): Phenol (440 μL, 5 mmol) and hexamethonium bis(tribromide) (1.7 g, 2.5 mmol) were mixed in a mortar by grinding at room temperature. The grinding continued for required time (Table 1) till the completion of the reaction (monitored by TLC). The reaction mixture was then transferred to a separating funnel, admixed with ethyl acetate (10 mL) and washed with water (2 x 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and then concentrated in rotary evaporator to obtain the reasonably pure *p*-bromophenol. However, for the purpose of analysis, the compound was further purified by passing it over a short column of silica gel and using a mixture hexane: ethyl acetate (9:1) as eluent to afford the product (**2a**) in 91% (790 mg) yield. The procedure was used all substrates giving liquid product.

Bromination acetanilide (1) to *p*-bromoacetanilide (1a): A mixture of acetanilide (**1**) (0.675 g, 5 mmol) and HMBTB (1.7 g, 2.5 mmol) was ground in a mortar by a pestle at room temperature. After disappearance of the starting material (monitored by TLC by taking a small amount of the mixture and dissolving it in ethyl acetate), the reaction mixture was transferred into a G_3 sintered funnel and washed with water (2 x 5 mL), and the solid was dried to yield 1.02 g (95%) of *p*-bromoacetanilide (**1a**). This procedure is applicable to all substrates giving product as a solid.

Regeneration of HMBTB (from reactions involving monobromination of substrates): The aqueous layer left after bromination reaction containing 1 equiv of hexamethonium bromide and 2 equiv of bromide (unused in the reaction) was concentrated to 5 mL. The concentrated aqueous layer was washed with ethyl acetate (2 x 5 mL) in a separating funnel to remove organic impurities (if any). The solution was then treated with KBr (2 equiv) and UHP (2 equiv) in 10 mL 4N H_2SO_4. The mixture on stirring for 30 min afforded 95% of hexamethonium bis(tribromide).

Regeneration of HMBTB (from the reaction of addition to C-C multiple bonds). Identical to the above, except 2 equiv of additional KBr and proportionately higher amount of the oxidant UHP were used.

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Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.