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Peroxometal-mediated environmentally favorable route to brominating agents and protocols for bromination of organics*

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Abstract: Higher-valent transition metals react with H_2O_2 to form peroxometallates, thereby activating the coordinated peroxide. Based on the reaction profiles of peroxometal species, environmentally acceptable newer syntheses of tetrabutylammonium tribromide (TBATB), Bu_4NBr_3, cetyltrimethylammonium tribromide (CTMATB), cetyl$(Me)_3NBr_3$, and tetraethylammonium tribromide (TEATB), Et_4NBr_3, have been developed from the reactions of the corresponding quaternary ammonium bromides with H_2O_2 and a catalytic amount of vanadium(V) or molybdenum(VI). Other transition metals capable of activating peroxide give similar results. The quaternary ammonium tribromides (QATBs) thus produced, especially TBATB and CTMATB, very efficiently act as clean and selective brominating agents for a variety of organic substrates. Very facile bromination of organic substrates, including aromatics, is also possible by tetrabutylammonium bromide (TBAB) Bu_4NBr, either promoted by V_2O_5–H_2O_2 or catalyzed by MoO_4^{2-}–H_2O_2. The scope of the protocols has been underscored, and the relevance to green chemistry has been highlighted.

PEROXOMETALS: THE HUB OF HALIDE OXIDATION

It has been a long-known fact that higher-valent transition metals interact with hydrogen peroxide to give very flamboyant reactions owing to the formation of peroxometal complexes in solution [1]. Such reactions are often very complicated particularly because of the formation of a number of complex species with varying compositions at different pH values of the reaction medium [2]. Peroxometal chemistry attracted a renewed interest some years ago especially because of an intrinsic biological interest in [3a–3e] and important catalytic activity [3f–3n] in important organic transformations [3] of peroxometallates. It was during the late 1970s through the early 1980s when solution studies engaged the attention of most of the workers in this field [4] that we began our work on the synthesis of peroxo compounds of metals such as Ti, V, Zr, and UO_2^{2+}, for instance. Our attention, in particular, was drawn a little more toward the peroxovanadium compounds leading to successful synthesis of a good number of simple and heteroligand di- and triperoxovanadates [5]. In this process, the importance of pH in the synthesis of such compounds and the scope of their widely varied reactions were realized. Guided by the burgeoning knowledge about the formation and transformation of complexes several reactivity studies were conducted by us [6] and by others [7]. These aspects were very comprehensively reviewed by Butler *et al*. a few years ago [7]. Our reactivity studies with peroxovanadates(V) involved a number of inorganic substrates [6], including bromide. Meanwhile, there was a breakthrough in this area in the early 1980s consequent upon the isolation of the vanadium-dependent haloperoxidase [3e] (VHPO).

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VHPOs are a class of enzymes that catalyze halide oxidations and act as catalysts in the marine biosynthesis of haloorganics [8]. Vanadium occurs in the enzyme in pentavalent oxidation state that activates hydrogen peroxide through coordination with the result that the activated peroxide functions as the oxidant for halide. The metal does not undergo redox cycling for the reduced vanadium deactivates the enzyme catalyst [8]. A number of oxo–peroxo complexes of vanadium(V) have been subsequently synthesized [9] in the quest of functional models for this enzyme. The central ideas that emerged out of many of these studies, including the solution experiments [10], are summarized as follows (Figs. 1–3):

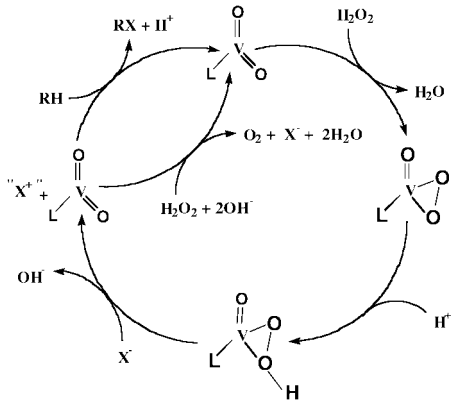


Fig. 1 Proposed catalytic cycle for the haloperoxidase.

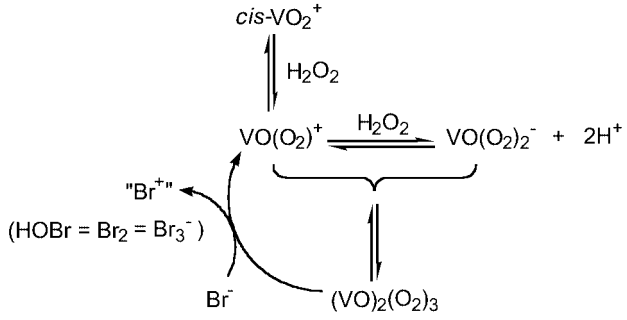


Fig. 2 Involvement of $(VO)_2(O_2)_3$ in Br^- oxidation.

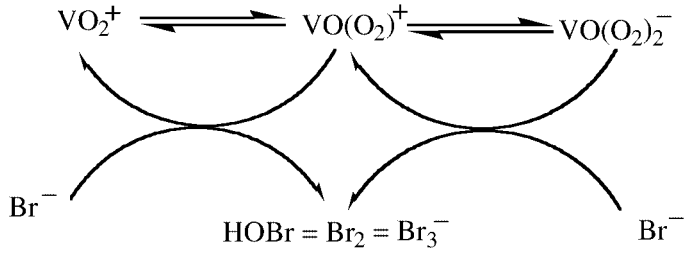


Fig. 3 VO_2^+-catalyzed oxidation of Br^- by H_2O_2.

The triperoxodivanadium(V) complex, $(VO)_2(O_2)_3$, (Fig. 2) is believed to be involved in the oxidation of Br^- [10a]. As a case in point, it appeared certain that either the red monoperoxo- or the yellow diperoxovanadate(V) complex [7], or an equilibrium thereof, generated in the reaction of oxovanadate(V) with H_2O_2 is responsible for the oxidation of bromide (Fig. 3).

QUATERNARY AMMONIUM TRIBROMIDES AND THEIR BROMINATION PROFILES

Intrigued by the above results, we sought to isolate the oxidized bromide species with an intention to characterize the product followed by investigation of its reaction profiles. Accordingly, the reaction of a series of quaternary ammonium bromides (QABs), were separately conducted with V_2O_5–H_2O_2, or $H_2MoO_4.H_2O$–H_2O_2 in the presence of a catalytic amount of acid, at *ca.* 5 °C leading to the isolation of yellow to orange–yellow quaternary ammonium tribromides (QATBs) in very high yields. The use of KBr or NH_4Br increases the yield of the product. The compounds can be recrystallized from acetonitrile to afford orange–yellow crystals with each of the compound showing a sharp melting point. QATBs, except pyridinium tribromide ($pyHBr_3$), are all stable and capable of being stored for prolonged periods. The involvement of peroxovanadate(V) in the reaction has been ascertained from the observance of the peroxovanadium charge-transfer (CT) band at 430 nm ($\varepsilon \sim 4300$) in aqueous V_2O_5–H_2O_2 solution [11].

$$\text{QAB} \xrightarrow[H_2O_2,\ \text{KBr or } NH_4Br]{V_2O_5 \text{ or } H_2MoO_4.H_2O/H^+} \text{QATB}$$

(Q = tetrabutylammonium, cetyltrimethylammonium, or tetraethylammonium, for instance.)

In representative procedures TBATB and CTMATB may be prepared as follows:

- TBATB: A solution of 2.75 mmol of V_2O_5 in 44.1 mmol of 30% H_2O_2 at *ca*. 5 °C on being reacted with 11 mmol of TBAB in 7 mL of water at ambient temperature produces yellow Bu_4NBr_3 (TBATB) in *ca*. 70% yield. The yield can be raised to 97% by the use of a catalytic amount of V_2O_5 and dilute H_2SO_4 and two molar equivalent of KBr. The product on recrystallization from acetonitrile affords orange–yellow crystals with a sharp melting point of 75 °C [11,12].
- CTMATB: This compound can be best synthesized by the aforementioned acid-catalyzed protocol using CTAB instead of TBAB. The yields of CTMATB are 93–96%. The microcrystalline product on recrystallization from CH_3CN provides orange–yellow crystalline CTMATB that melts at 87 or 88 °C.

It may be relevant to mention in passing that the corresponding tetraethylammonium tribromide, Et_4NBr_3 (TEATB), synthesized in an analogous manner has a melting point of 85 °C. One of the very rapid ways of characterization of tribromides is by recording their electronic absorption spectra. An intense band at *ca*. 267 nm is characteristic of tribromide(Br_3^-) [13]. It has also been observed by us that both TBATB and CTMATB exhibit characteristic (Br_3^-) [14] IR bands at *ca.* 170(ν_1) and *ca.* 191(ν_3) cm^{-1}, and laser Raman signals at *ca.* 145(ν_1) and *ca.* 165(ν_3) cm^{-1}. Interestingly, the X-ray structure of TBATB (Fig. 4) [15] shows that the compound crystallizes in the monoclinic space group C2/c, and the Br–Br–Br is totally symmetrical with the Br2a–Br1–Br2 being 180°. The two Br–Br distances are identical [2.533(3)°].

Thus, it has been demonstrated that the quaternary ammonium tribromides (QATBs) like TBATB, CTMATB, and TEATB can be synthesized in very high yields in an environmentally safer way, and stored stable for a prolonged period. In the meanwhile, our attention was drawn to bromination of organic substrates, particularly aromatics, that has garnered a significant amount of attention in recent years [8,16] due to the commercial importance of such compounds as potent antitumor, antibacterial, antifungal, antineoplastic, antiviral, and antioxidizing agents [8] and also as industrial intermediates for manufacture of speciality chemicals, pharmaceuticals, and agrochemicals.

Unfortunately, the hazards associated with traditional bromination are not trivial and cannot be overlooked [17]. Environmental problems caused by the use of detrimental chemicals and solvents [18] in classical brominations and anticipated legislations against their use are some of the major concerns. Consequently, what is needed is a protocol that would be environmentally clean and yet efficient, site-selective, operationally simple and cost effective. Selective bromination of aromatics, a process of great commercial importance, has also been a case in point. Having synthesized by the new protocol, the efficacy of the QATBs as brominating agents was ascertained. The results of such experimentations involv-

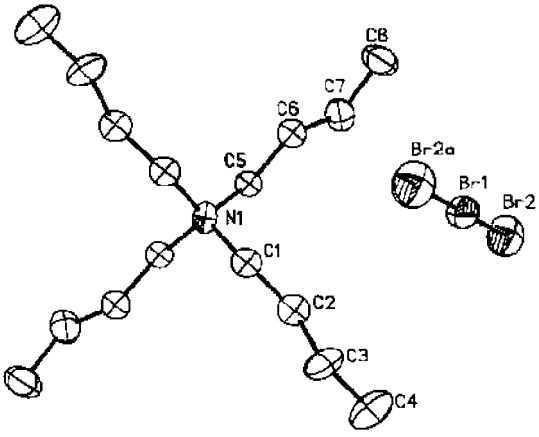


Fig. 4 Crystal structure of tetrabutylammonium tribromide, TBATB.

Table 1 Bromination of aromatics and some other substrates with TBATB.

Substrate (entry)	Substrate:TBATB	Product(s)	% yield
aniline (1)	1:1	p-bromoaniline (1a)	60
aniline (1)	1:3	2,4,6-tribromoaniline	65
phenol (2)	1:3	2,4,6-tribromophenol (2a)	60
anthracene (3)	1:1	9-bromoanthracene (3a)	70
anthracene (3)	1:2	9,10-dibromoanthracene (3b)	55
phenanthrene (4)	1:1	9-bromophenanthrene	46
benzene (5)	1:1	bromobenzene	40
imidazole (6)	1:3	2,4,5-tribromoimidazole (6a)	68
allyl alcohol (7)	1:2	2,3-dibromopropanol	72
styrene (8)	1:2	vic-dibromostyrene	62
chalcone (9)	1:2	threo-dibromochalcone	65
cinnamic acid (10)	1:2	2,3-dibromo-3-phenyl propanoic acid	60
acetophenone (11)	1:1	bromomethyl phenyl ketone	46
3-(4′-benzyloxyaryl)-1-(4′,6′-dimethoxy-2′-hydroxyaryl)propenone (12)	1:1	3-(4′-benzyloxyaryl)-1-(5′-bromo-4′,6′-dimethoxy-2′-hydroxyaryl)propenone **(12a)**	70
12	1:3	1-(5′-bromo-4′,6′-dimethoxy-2′-hydroxyaryl)-3-(4′-benzyloxyaryl)-2,3-threo-dibromopropanone (12b)	55

ing TBATB and CTMATB are summarized in Table 1 and Table 2, respectively. The reactions were conducted in acetonitrile due to environmental safety requirement, although similar reactions are possible in dichloromethane as well.

What is evident from the product profile analysis is that both the reagents are very efficient with CTMATB having an edge over TBATB in terms of higher yields of the products and lesser cost of the reagent. Unfortunately, tetraethylammonium tribromide, Et_4NBr_3 (TEATB), did not so far work satisfactorily. Although bromination of similar substrates seems to be possible with TEATB, but the reactions generally take longer time with yields of the products being comparatively much less. Importantly, while investigating their thermal stability by thermogravimetric (TG) experiments, it was observed that each of TBATB and CTMATB loses Br_2 as the tail fragment at 265–267 °C whereas TEATB does not seem do so under analogous experimental conditions (Fig. 5). The implication of this observation is believed to be a manifestation of TEATB's being a weaker brominating reagent compared to TBATB and CTMATB.

The results of room-temperature brominations of aromatics including polycyclic hydrocarbons, sensitive substrates such as imidazole, allyl alcohol, and ketones as well, as some other substrates are set out in Tables 1 and 2. Selective brominations of activated aromatics such as aniline and polycyclic

Table 2 Bromination of aromatics and some other substrates with CTMATB.

Substrate (entry)	Substrate:CTMATB	Product(s)	% yield
1	1:1.1	2,4-dibromoaniline	65
2	1:1.1	4-bromophenol	70
3	1:1.2	**3a**	87
6	1:3	**6a**	55
o-cresol **(13)**	1:1.1	4-bromo-*o*-cresol **(13a)**	67
p-cresol **(14)**	1:1.1	2-bromo-*p*-cresol **(14a)**	71
phluroglucinol **(15)**	1:1.1	2,4-dibromophluroglucinol	58
o-nitroaniline **(16)**	1:1.1	4-bromo-*o*-nitroaniline	
methyl-3-phenyl-2-propenoate **(17)**	1:1.2	2,3-dibromo-methyl-3-phenyl-2-propanoate	85
1,3-diphenyl-2-propen-1-one **(18)**	1:1.5	2,3-dibromo-1,3-diphenyl-2-propan-1-one	78
1,4-(4′-methoxy-phenyl)-diphenyl-3-propen-1-one**(19)**	1:1.5	2,3-dibromo-1,4-(4′-methoxy-phenyl)-diphenyl-3-propan-1-one	92
16-dehydro pregnonalone acetate **(20)**	1:1.2	16,17-dibromo-pregnonalone-acetate	67

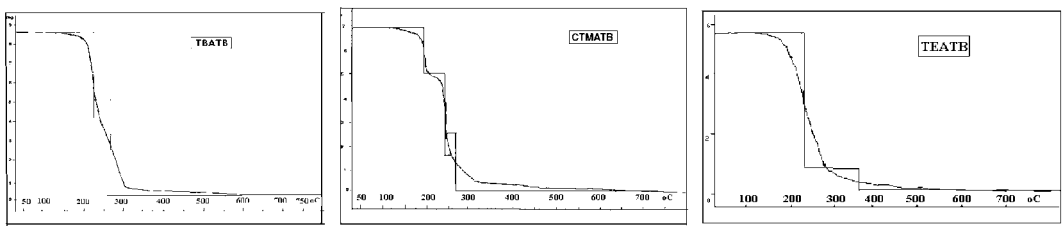
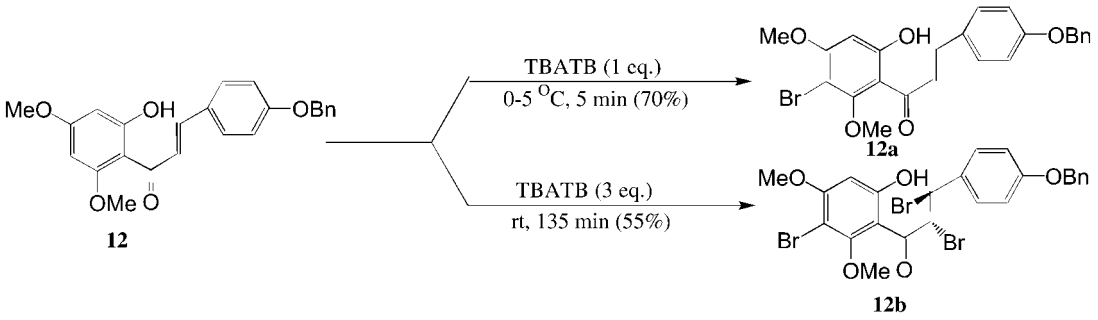


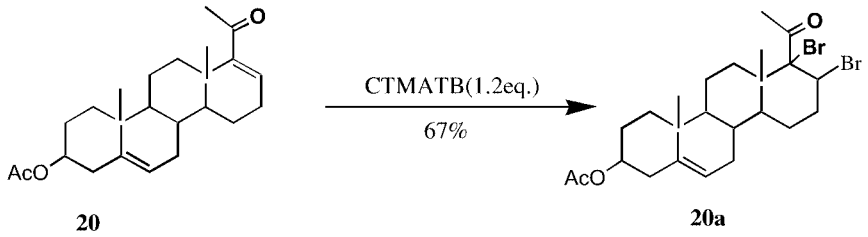
Fig. 5 Thermograms of TBATB, CTMATB, and TEATB.

aromatics such as anthracene and phenanthrene, bromination of unreactive rings like benzene and a sensitive substrate, for instance, imidazole are noteworthy. The reagents also allow easy double bond bromination under mild reaction conditions. Equally important if not more are the following reactions:

The selective bromination of an activated aromatic ring in the presence of an olefinic double bond by TBATB: For instance, substrate **12**, an important synthetic precursor for naturally occurring flavonoids (c.f. vitexin) [11], on being reacted with an equimolar amount of TBATB gave **12a** as the exclusive product, while a similar reaction when conducted with **12**: TBATB at a molar ratio of 1:3 yielded **12b**.



And selective bromination of a conjugated double bond in presence of an isolated double bond by CTMATB as exemplified by the transformation of substrate **20** to **20a** is a unique case of the kind.



PEROXOMETAL-MEDIATED GENERATION OF Br_3^- *IN SITU* LEADING TO ENVIRONMENTALLY FAVORABLE SYNTHETIC PROTOCOLS FOR BROMINATION OF ORGANIC SUBSTRATES

Bromination by tetrabutylammonium bromide (TBAB) promoted by V_2O_5–H_2O_2

Taking cues from the knowledge of activity of vanadium bromoperoxidase (VBrPO) [16] as well as our previous experience of the reactivity of peroxovanadium systems [6a,19], an environmentally acceptable bromination protocol has been developed [16] involving V_2O_5 as a promoter, H_2O_2 and TBAB as the sources of active oxygen and bromide, respectively. The solvent of choice is CH_3CN/H_2O. The promoter (V_2O_5) and the oxidant (H_2O_2) are both environmentally safe chemicals.

The strategy has been based on (i) activation of dioxygen by the interaction of H_2O_2 with V(V) leading to peroxovanadium(V) species (λ = 430 nm) in solution followed by (ii) oxidation of Br^- by the peroxovanadium(V) intermediate ultimately leading to the formation of Br_3^- (λ = 266 nm) as the active brominating agent, and finally (iii) bromination of organic substrates to afford bromoorganics (Fig. 6). Ideally, a 1:3:0.5:16 substrate:TBAB:V_2O_5:H_2O_2 stoichiometry appeared to be optimal and that CH_3CN/H_2O (1:1) solvent gave very good yields. The reactions were conducted at *ca.* 5 °C and the desired products obtained in high to very high yields (Table 3).

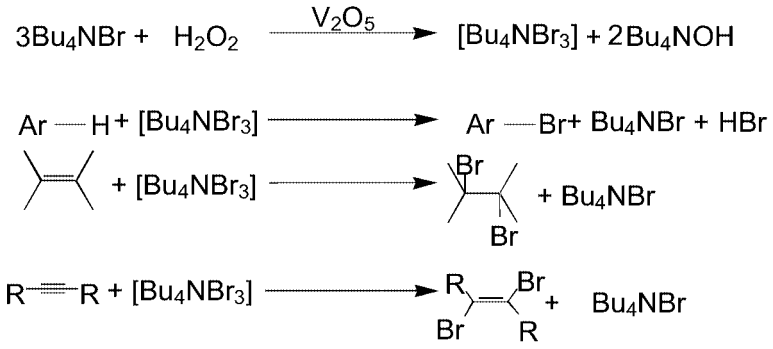


Fig. 6 Generation of TBATB *in situ* and bromination of organic substrates.

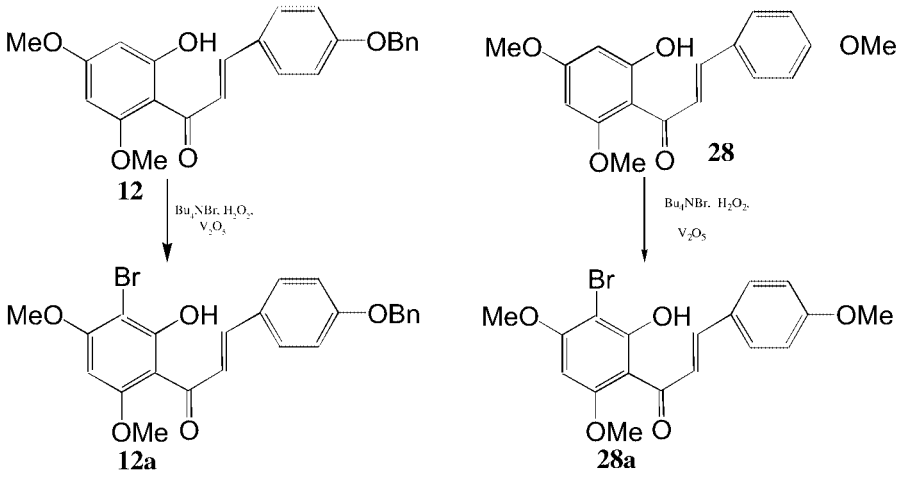
Table 3 Bromination of aromatics and some other substrates with TBAB and V_2O_5–H_2O_2.

Substrate (entry)	*t*/h	Product(s)	% yield
1	0.5	**1a**	82
acetanilide **(21)**	2	4-bromoacetanilide	92
13	1.5	**13a**	92
m-cresol	0.5	4-bromo-*m*-cresol	60
2	1	**2a**	98
β-naphthol **(22)**	1	1-bromo-β-naphthol	76
3	1	**3b**	93
cyclohexene **(23)**	2	1,2-dibromocyclohexane	70
crotyl alcohol **(24)**	2	2,3-dibromo-1-butanol	60
2-butyne-1, 4-diol **(25)**	1.5	2,3-dibromo-2-butene-1, 4-diol	46
cyclohexanone **(26)**	2	2-bromocyclohexanone	52
4-hydroxycoumarin **(27)**	1	α,α-dibromo-*o*-hydroxy acetophenone	55
12	1	3-(4′-benzyloxyaryl)-1-(3′-bromo-4′,6′-dimethoxy-2′-hydroxyaryl) propenone **(12a)**	72
3-(4′-methoxyaryl)-1-(4′,6′-dimethoxy-2′-hydroxyaryl)propenone **(28)**	1	3-(4′-methoxyaryl)-1-(3′-bromo-4′,6′-dimethoxy-2′-hydroxyaryl) propenone **(28a)**	70

Significantly, no extra addition of acid is required by this method. The intrinsic acidity originating from the reaction of V_2O_5 with H_2O_2 not only neutralizes the hydroxide in Fig. 6 but also maintains the reaction medium acidic with a pH value of 2.1, as observed. Apparently sufficient acid could be generated in the process for the use of 0.5 molar equivalent of V_2O_5 to allow for Br^- oxidation by the peroxovanadium(V) species formed in the reaction. The methodology is capable of being made catalytic with KBr as the consumable source.

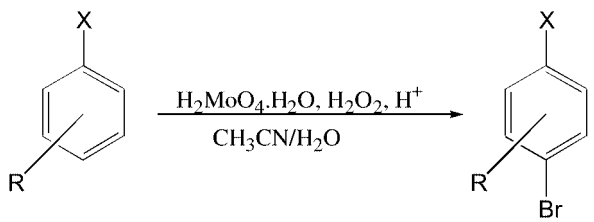
Quite intriguing is the regioselective bromination of activated aromatics as given in Table 3. The efficacy of the methodology lies also in the bromination of alkene and alkyne as exemplified by the facile bromination of cyclohexene, crotyl alcohol, and 2-butyne-1,4- diol, respectively. The conversion of cyclohexanone to 2-bromocyclohexanone in high yield might be a paradigm for the synthesis of α-bromoketone. Quite interesting is the transformation of 4-hydroxycoumarin to α,α-dibromo-*o*-hydrox-

yacetophenone, an unprecedented reaction until we reported the one [16]. Also important is the selective bromination of the activated aromatic ring in presence of an enone as shown below.



Bromination by TBAB catalyzed by MoO_4^{2-}–H_2O_2 and H^+

Although the protocol discussed above is a versatile one and very safe to operate we were little concerned about the use of more than a catalytic amount of V_2O_5 (0.5 molar equiv.) in the methodology. One of the reasons for the use of a relatively higher amount of V_2O_5 was to generate enough acidity from its reaction with H_2O_2 [16] so that the reaction solution attained a suitable pH value to allow for Br^- oxidation. It has been now possible to show that **TBAB** can very effectively brominate a variety of substrates catalyzed by MoO_4^{2-}–H_2O_2 and H^+. Catalyst optimization experiments revealed that a maximum amount of 0.2 molar equivalent of each of $H_2MoO_4.H_2O$ and $HClO_4$ is good enough to produce the desired products in very high yields. In order to compare the efficacies of the two protocols discussed herein, the substrate profiles and the solvent system were maintained the same. What has emerged out of this investigation is that the reactions appear to be equally facile and the methodology is versatile with yields of products being higher in many cases. The product selectivity with this methodology is also very high.



The procedures can be made catalytic using KBr or NH_4Br as the consumable source. Similar brominations are possible by cetyltrimethylammonium bromide (CTMAB) in lieu of TBAB.

In conclusion, it must be admitted that the results of our endeavour in the field of peroxometal chemistry provided us a lead to develop a clean method for the synthesis of quaternary ammonium tribromides (QATBs) capable of brominating a wide variety of organic substrates including aromatics in a safer way. Reactions of peroxometal intermediates can as well be exploited to generate an active brominating species (Br_3^-) *in situ* which can also perform bromination of organic substrates very efficiently without compromising with the environmental acceptability.

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