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Synthesis of cetylpyridiniumtribromide (CetPyTB) reagent by noble synthetic route and bromination of organic compounds using CetPyTB

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A B S T R A C T

Cetylpyridiniumtribromide (CetPyTB) has been produced by a noble synthetic path protocol and its reactivity studied. Result indicates that the reagent shows good capability as a brominating agent for carbon/electron-rich heterocyclic aromatic compounds in addition to an efficient catalyst for acetylation of the alcohols, therefore proving it to be a note-worthy addition to the current organic tribromide reagents.

Capsule Summary: The synthesis and characterization of cetylpyridiniumtribromide (CetPyTB) by noble synthetic route and bromination of organic compounds using CetPyTB is reported.

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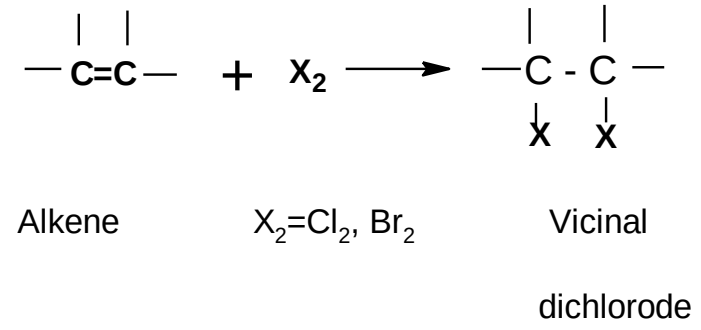
INTRODUCTION

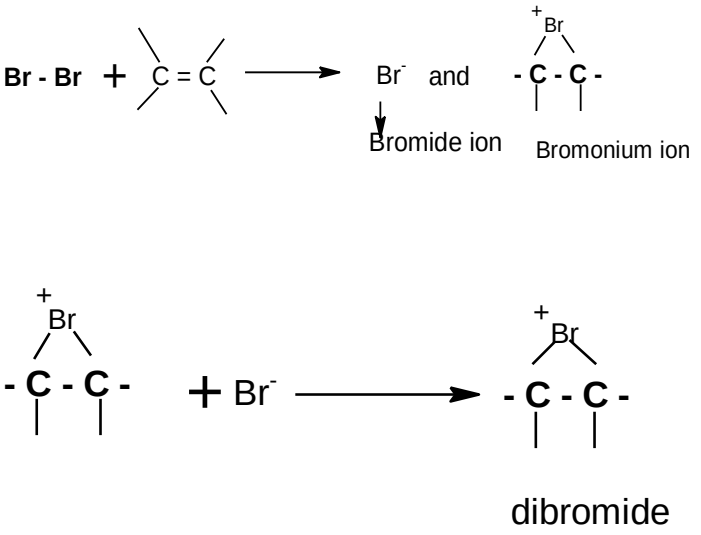
Previous readings of organic transformation shows, organic ammonium tribromides are becoming a lesser yet important group of reagents. Because of their easiness of formation, tenderness, immense versatility, these reagents have become quite widespread and a number of research data is available discussing the importance of these reagents in various types of transfigurations (Jackisch, 2000). The effects of electrolyte, pH, and surface preparation on the surface excess and chemical kinetics are reported (De la Mare, 1976). At all other concentrations and even at the Critical Micelle Concentration when electrolyte is present the adsorption is complete within few minutes.

Cetylpyridiniumtribromide synthesis and use as a interesting antiseptic/disinfectant, deodorant, laboratory reagent, and surfactant may result in its discharge to the environment through various waste stream flows (Podgorsek et al., 2009). If unconfined to environment, cetylpyridiniumtribromide will occur in the particulate phase in the ambient atmosphere as an ion. Particulate-phase cetylpyridiniumtribromide will be distant from the atmosphere by wet and dry deposition. If released to soil, cetylpyridiniumtribromide is expected to have moderate litheness based upon an estimated Koc of 240. Cetylpyridiniumtribromide is expected to biodegrade rapidly in aerobic soil and water environments based on studies using sewage; rates of biodegradation increased with acclimation of the microbial population (Pingali et al., 2010). Our research focused on method development for bromination using new Eco friendly reagents. The U.S. E.P.A. has reviewed a large body of literature concerning the reaction of organic compounds in different industrial processes (Beckmann et al., 2013; Bedford et al., 2013; Cerichelli et al., 2006).

The direct halogenation system Br_2 doesn't react at low temperature in noticeable manner with Cl_2. But in presence of catalytic system such as Al-Hg, C_6H_5N or Fe, reaction process takes place readily, the monohalogenated derivative afforded as a main product in first instance. Mostly the p-isomers of di-substituted products were obtained if we increase the proportion



Step 1



Step 2:

Scheme 1: Mechanism of addition of halogens

of halogen. Few such typical procedures are known like bromobenzene. The catalyst use helps to increase electrophilic activity of the halogens. The iodination can be carried out by using the oxidizing agent because iodine is less reactive among all halogens. The nature of electrophile which functions as I^+ when using fuming nitric acid as a catalyst, I^+ thought to be $[O=N (I) OH]^+$. $CuCl_2$ is being recently used as a source of oxidant in the presence of Aluminium Chloride. In both the methods, iodobenzene was obtained in good yield but the later method is more suitable for the iodination of alkylbenzenes. Aromatic hydrocarbons which are condensed easily react with electrophilic reagent. Example Naphthalene is readily brominated in solution in carbon tetrachloride without using any catalyst.

In side chain halogenation of toluene using chlorine or bromine, took place with the exposure to sunlight or other bright light. The reaction does not require any catalyst. The first chlorine atom and the reaction results in the formation of benzyl chloride first then benzylidene chloride and at last benzotrichloride are formed. The replacement of hydrogen atom from an aromatic compound by a chloromethyl (CH_2Cl) group is

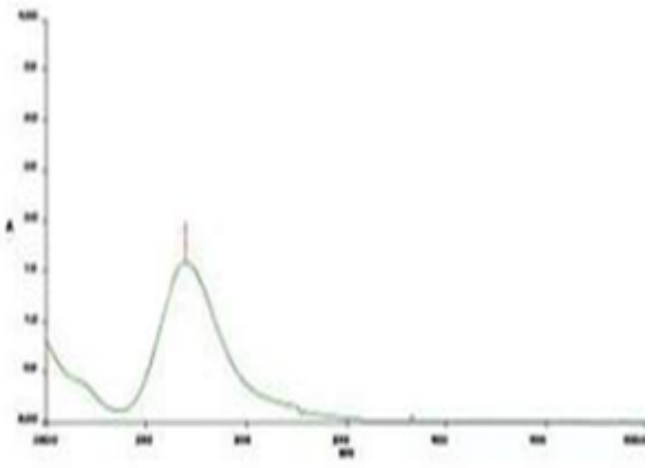


Fig. 1: Microelectronic spectrum range of CetPyTB

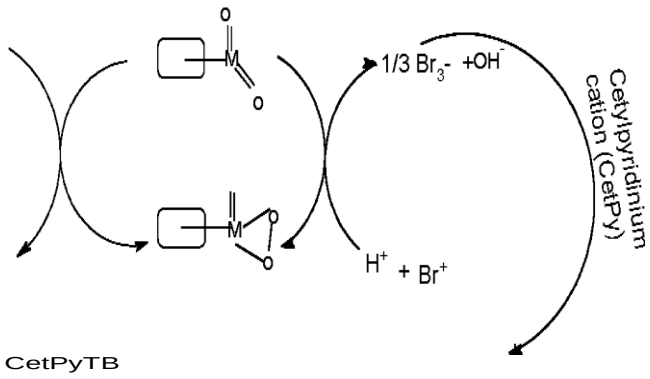


Fig. 2: CetylpyridiniumTribromide Synthesis Path (M = Mo and O = any ligand other then Peroxo)

Table 1: Boosted Stoichiometry for Synthesis of the CetPyTB

CeTPyB (g)	Na_2MoO_4 (g)	H_2O_2 30% (mL)	KBr (g)	1*M* H_2SO_4 (mL)
13.62	0.38	44.0	41.2	50

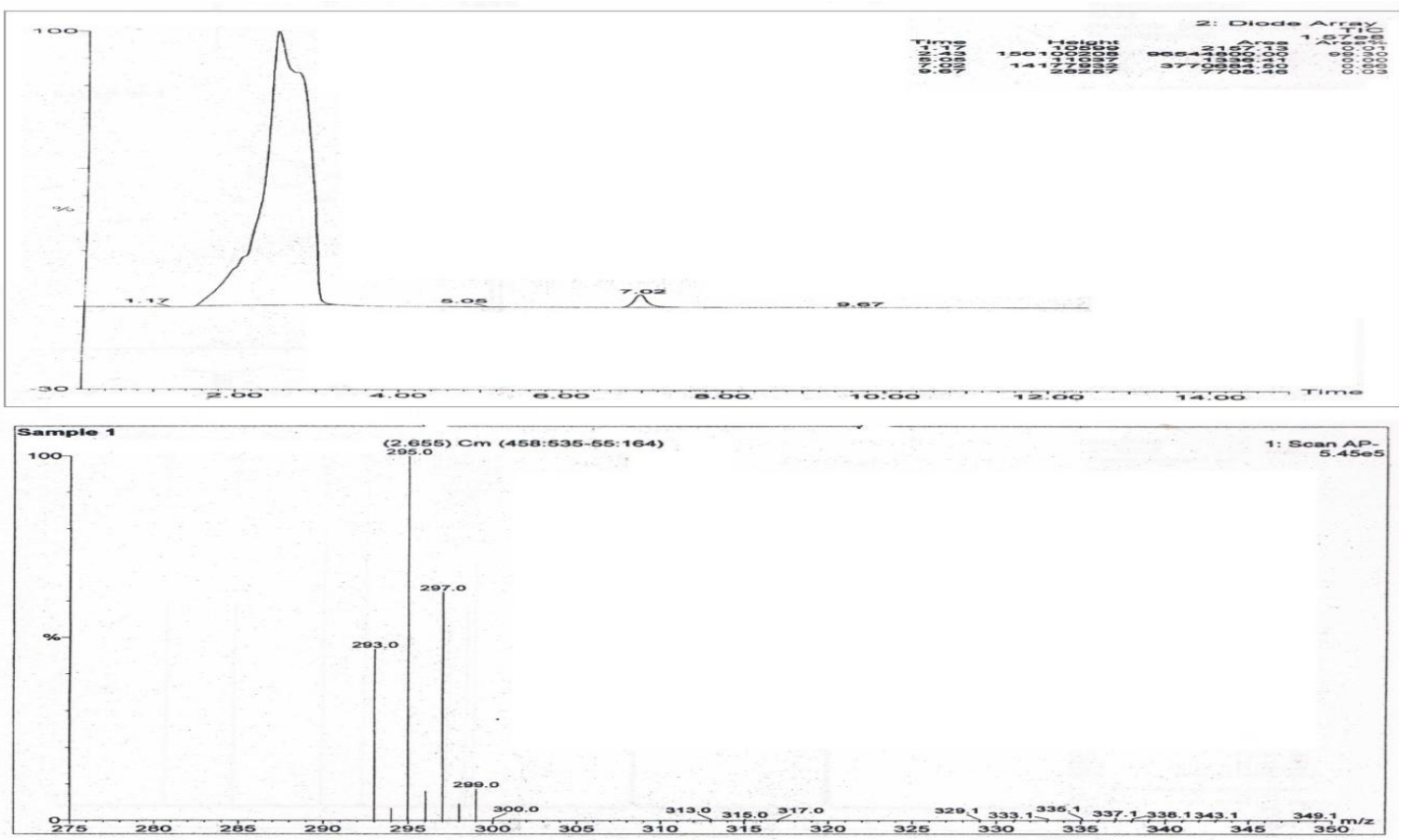


Fig. 3: LC-MS of 3,5-dibromosalicylic acid (**1**)

called chloromethylation. Originally the reaction consists of the interation of formaldehyde and hydrogen chloride in the presence of a catalyst like aluminium chloride or zinc chloride with an aromatic system (Blanc chlomethylation reaction).

In case of aromatic compounds, free amino group strongly activate the aromatic ring for the electrophilic attack and aromatic substitution of amines that ultimately results in polysubstitution. The aniline and o-toluidine undergoes through iodination using iodine in the presence of sodium hydrorbonate or calcium carbonate resulted in substituent entering the para position to the amino group. Further other chloro compounds are also used for the mono-chlorination of aromatic amines. Examples:- NCS which largely restricted the chlorination of aniline to monosubstitution. Halogenation of acetic acid using gaseous chlorine in the presence of red phosphorus results in formation of mono, -di, and triacetic acid (CO_2Cl) CO_2H, $CH_2Cl.COOH$ and $CCl_3.CO_2H$ respectively. However on the other hand Bromination of acetic acid is highly selective and only α-bromo acetic acid is obtained when reaction is carried out in the presence of reagent such as red phosphorous of phosphorous trichloride or tribromide(Halogenation of carboxylic acid).

Halogenation of aqueous solution of phenol with bromine water yields in precipitate of 2,4,6 tribromophenol. However the mono-bromination of phenol with can be achieved by using the solutions of bromine in non polar solvents like carbon disulphide and carbon tetrachloride at very low temperature ie. 0-5 ^oC and the product obtained is exclusively the para isomer. There are various methods/procedures for the preparation of aromatic halogen compounds including direct halogenation which is done either by substitution in the nucleus or by the substitution in the side chain of aromatic compounds, chloromethylation, or by replacement of a diazo group by the halogen and through replacement of hydroxyl group by the halogen.

Addition of halogens: The unsaturated organic compounds are readily converted in to saturated compounds when reacted with halogens (chlorine, bromine, iodine). However iodine reacts very slowly. The addition of halogens readily proceeds at room temperature or below by mixing together the two reactants ie. unsaturated compounds and halogens. The high temperature and excessive amount of halogens leads to conditions where substitution might become an important side reaction.

Mechanism of addition of halogens

Halogens are attached to the unsaturated compounds through electrophilic addition that involved two steps (Scheme 1). In the first step, a cation is formed but in most cases this cation is not a carbon but something now ie. halonium ion. Example, In case of bromine firstly bromine is transferred from bromine molecule to the unsaturated compound (for example alkene) in such a way that is attached to both the carbon forming a cyclic Bromonium ion. This step does not represent electrophilic addition. However in this the Bromine is transferred as positive bromine and left newly formed bromide ion. In second step this bromide ion reacts with the bromonium ion and results in the formation of product ie. dibromide. The insertion of bromine atom into the

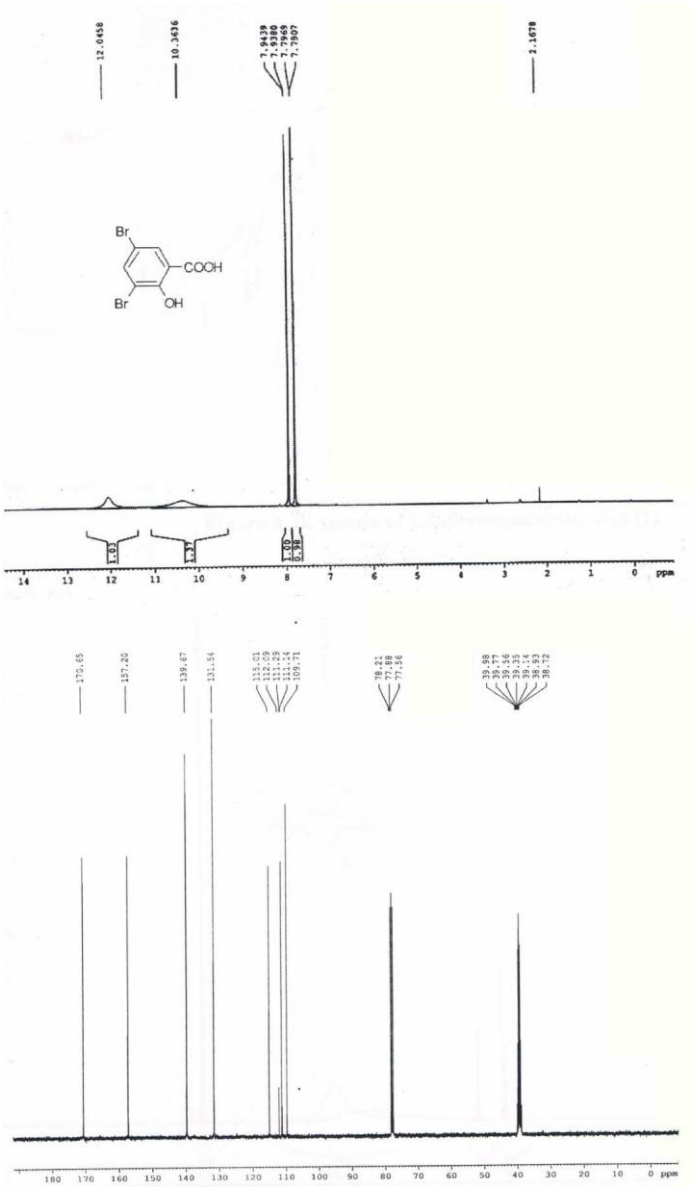


Fig. 4: ^{1}H and ^{13}C-NMR spectra of 3,5-dibromosalicylic acid (**1**)

organic molecule with its simultaneous oxidation is called oxybromination. The bromonium ion (Br^{+}) along with counter ion (mainly OH^{-}) is the main active species in oxybromination reactions. The bromonium ion provided directly in the solution by brominating reagent or alternately it is generated in-situ from the oxidation of bromide (Br-) using suitable oxidant in particular reaction conditions. The later strategy is more favorable than former one and it is widely utilized. The oxybromination reactions are vital for the synthesis of various important bromoderivatives: bromohydrins, α-bromoketones and α,α-dibromoketones as well as for other useful organic synthesis.

In the face of changing environmental demands and environmental-friendly organic syntheses, clean and green organic reaction methods which do not use any environment hazards organic solvents are fortified and are in abundant demand. Further drawbacks of the established bromination methods include their use of harmful reaction chemicals, complicated examination methods, organic solvents or uncommon and costly chemicals and solvents. Consequently, the bromination reaction has been still very attractive attention to develop the more practical and eco-friendly method suitable for commercial-scale/industrial-scale synthesis. These explanations heighten the flexibility of Br_2 as an economical, widely available and most commonly employed starting material.

Therefore, to reconnaissance the chosen commercial and industrial-bromination reaction conditions with lowest byproducts generation, as well as eradication of the consumption of hazardous oxidants, metal catalysts, strong acids and organic solvents, we have advanced a green method employing the liquid Br_2 as brominating agent for the approach to direct bromination of heterocyclic aromatic compounds in micellar aqueous medium. Aq. solution of sodium lauryl sulphate (SLS) at its CMC catalyses the fast direct regioselective bromination of structurally-diverse, industrially-important aromatic compounds at 25±1 ˚C within a few minutes of reaction time.

EXPERIMENTAL

Reagents and Analytics

All solvents, chemicals and reagents were taken from commercial sources and used without any further purification. Reaction progress was monitored by thin layer chromatography (TLC) using Silica G-60 UV254s glass plates from Merck, Germany or on TLC‘s prepared from silica-gel fine powder layered on glass plates. Condenser and reaction flask heated in oil bath at preferred temperature on a magnetic stirrer which provides stirring and heating the reaction mixture (Gopinath et al., 2002). The solvents used for the abstraction of products were removed under abridged pressure (where-ever required) using Buchirotavapour. The spectra were logged in $CDCl_3$, MeOD and DMSO as solvents unless otherwise noted (Eberlin et al., 2002; Firouzabadi et al., 2003). Chemical shifts are described in parts/million relative to tetramethylsilane as an internal standard, for ^{1}H and ^{13}C NMR spectra. The ^{1}H and ^{13}C chemical shifts were relating to last solvent signal (Gopinath et al., 2002).

Optimization of Synthetic Protocol of the CetPyTB

A number of reactions were carried out to reach the optimum amount of all the reagents used. Table 1 gives the finest ratio of the chemicals required for the synthesis of Cetylpyridinium Tribromide. One of the most reliable and prompt ways of characterization of tribromide is by recording their electronic absorption spectra (Fig. 1). Br_3^{-} reveals characteristic signature at ca. 264 nm with a assume at ca. 382 nm due to the shifts σ^{-}-σ^{*} and $\pi - \pi^{*}$ respectively. The σ^{-}-σ^{*} and $\pi - \pi^{*}$ transitions for compound under discussion gave value 267.2 nm with a low intensity confirm the uniqueness of the reagent.

Procedure for preparation of CetPyTB using Na_2MoO_4 and hydrogen peroxide

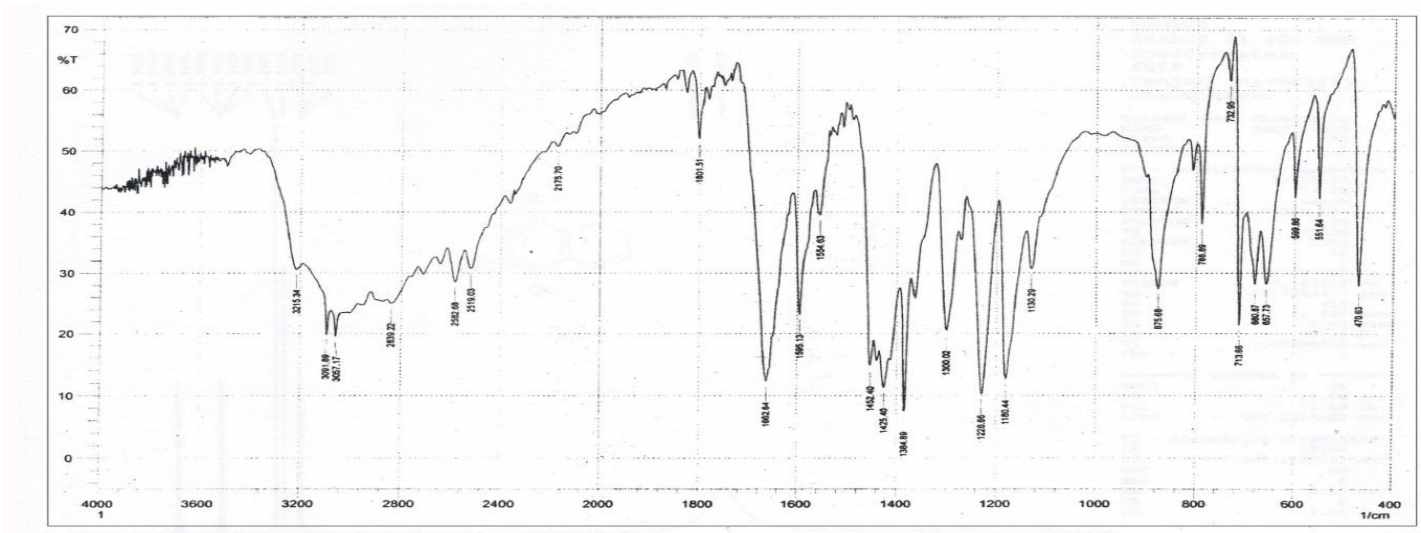


Fig. 5: IR spectra of 3,5-dibromosalicylic acid (**1**)

An amount of 22 g (0.1068 m mol) of Na_2MoO_4 was added to 54 ml of 30 per cent hydrogen peroxide occupied in a pre-cooled 250 mL beaker (in ice-cold condition) as the reaction is exothermic. The reaction mixture was stirred at 0-5 °c temperature in an ice water bath till all the sodium molybdate Na2Mo04, dissolved and the solution turns reddish-brown. To it was added a solution of 9.78 g (82.14 mmol) of KBr and 10.56 g (27.48 mmol) of CetPyB, liquefied in 70 mL of water. 100 mL of 1M sulphuric acid added to this in small percentages. Magnetic stirring was sustained for a further period of 2h at ice-water temperature. The yellow product thus molded was isolated by force filtration using whatsmam 1 filter paper. The compound was then dehydrated in desiccator using anhydrous $CaC1_2$ as desiccant. A profound orange yellow product was found on recrystallization with acetonitrile. The yield of the recrystallized product was 90.2 per cent.

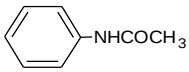
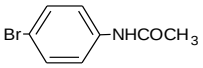
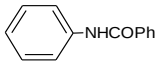
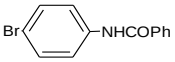
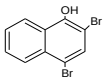
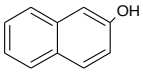
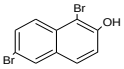
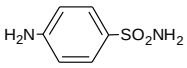
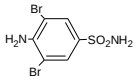
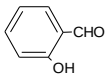
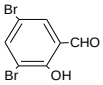
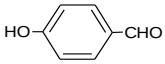
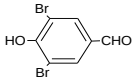
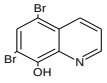
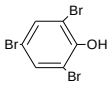
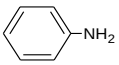
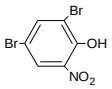
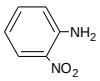
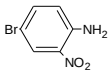
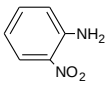
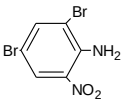
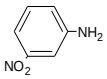
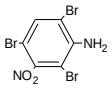
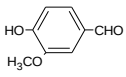
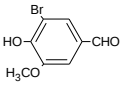
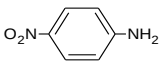
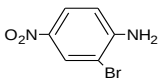
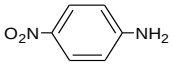
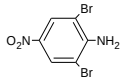
Influence of quantity of reagent on the end product yield and melting point of 3, 5-DBSA

The amount of ammonium salt plays a key role in end product yield. The finest yield (96 per cent) and the preferred melting point (226-229 °C) of 3,5-Dodecylbenzenesulfonic acid are obtained when 23 mg of CetPyTB was employed in the bromination of salicylic acid (10 mmol) by molecular Br_2 (20 mmol) as a brominating agent. At 5 mg and 10 mg of CetPyTB, the yield of 3, 5-DBSA, were 91 and 93 percent correspondingly. If we change the amount of CetPyTB upto 0.50 gram and 1 gram, there is no noticeable effect on the yield of end product, melting point and quality of end product.[16-21] To observe the opportunity of present bromination method, we, therefore, functional similar reaction conditions to a selection of aniline and phenol byproducts with strong electron-withdrawing groups (EWGs) such as -COOH, -NO_2, and -CHO as examples of pharmaceutical intermediates (Table 1). The different aromatic substrates brominated by the same method, may have dissimilar solubilization effect in the micellar aggregation after CMC, as specified by their partition coefficient (P) log values. Though, the rate of reaction is very fast with the present reagent system and the lipophilic nature of aromatic substrate does not play any significant role in the process.[21-23] The ingestion of Br_2 in the reaction process is instantaneous and most of the reactions are completed within 10-15 minutes of short reaction time lagged by adding of Br_2 into the round-bottom flask, providing the brominated products in >99 HPLC purity yield.

The bromination of Acetanilide **2** and benzanilide **3** were successfully done, to their analogous p-brominated products in great yields (Adimurthy et al., Bedekar et al., 2005; 2006; Qtera, 2003; Stropnik et al., 2008). Which actually specify that the number of entering Br_2 atoms as well as position of the electrophilic attack can be regulated by directing the ratio of Br2: substrate, i.e. for mono- 1:1, for di- 2:1 and 3:1 for tribromination of aromatic compounds (Naik et al., 2003; Wang et al., 2008; Yin et al., 2007). Traditional direct bromination method using Br_2 in conc. hydrogen bromide or any organic solvent is not very discriminatory and repetitively results in a composite mixture of mono-, di-, tri-, and even tetra-brominated products. $Br_3C_6H_2NH_2$ (Table 2, entry 4), an intermediate for Bulk drugs, agrochemicals and pharmaceuticals, and $Br_3C_6H_2OH$ (Table 2, entry 9), a reactive flame retardant were achieved in decent yields using 3 molar equivalents of Br2. $C_{10}H_7BrO$ (1-napthol 6) and $C_{10}H_7BrO$ 2-napthol 7 progressed with decent reactivity affording green synthesis of $C_{10}H_6Br_2O$ (93 percent) and $Br_2C_{10}H_5OH$ (91 percent) after 15 minutes, correspondingly.

By same route it also has been observed that oxine 9 and sulphanilamide 8 could also be promptly dibrominated affording 5, 7- dibromooxin ($C_9H_5Br_2NO$) and $C_6H_6Br_2N_2O_2S$ (3, 5-dibromosulphanilamide), (a potent inhibitor of most human fungal pathogens) in yields of 99 and 97 percent, respectively. Pharmaceutically-important aromatic aldehydes were promptly brominated at 23-25° temperature in great yields (Table 2). Another anthelmintic or antibacterial, 2, 4-dibromo-6-nitrophenol ($C_6H_3Br_2NO_3$) was attained in outstanding yield within 20 minutes from 2-nitrophenol "$O_2NC_6H_4OH$" (Table 2, entry 11). The bromination of 2-nitrophenol ($C_6H_3Br_2NO_3$) is

Table 2: Bromination of various aromatics in aqueous media using CetPyTB

Entry	Substrate	Product	Time/min	Yield (%)	Mp/°C (lit.)
1.			10	98	167(165-169)
2.			25	92	200(200-202)
3.			15	93	105(105-107)
4.			20	95	104(105-107)
5.			20	95	235(235-237)
6.			15	96	80(80-84)
7.			20	90	183(181-185)
8.			15	98	200(198-200)
9.			15	91	92(92-94)
10.			25	93	120(120-121)
11.			20	95	114(116-117)
12.			15	94	108(110-113)
13.			20	97	127(127-130)
14.			20	96	102(100-103)
15.			15	92	166(164-166)
16.			15	90	102(102-104)
17.			20	94	204-208 (206-208)

difficult using dualistic reagent system (Br2/Cetyltrimethylammonium bromide/Cs2.5H0.5PW12O40). But in case if anilines containing deactivated groups, regioselective bromination is not an easy task and in most of the

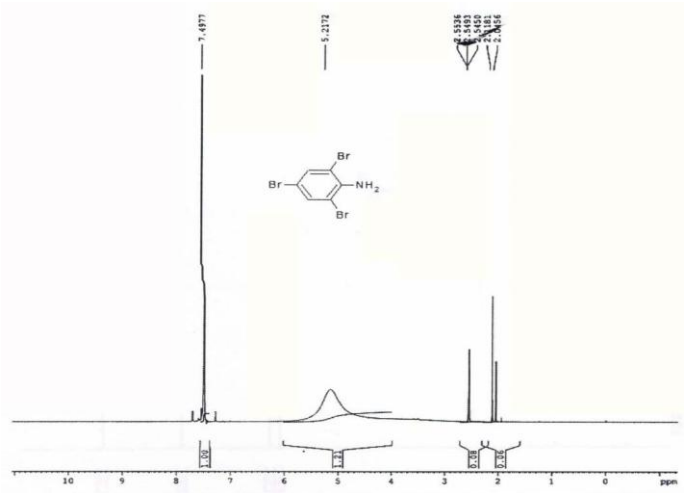


Fig. 6: ^{1}H-NMR spectra of 2, 4, 6-tribromoaniline (**4**)

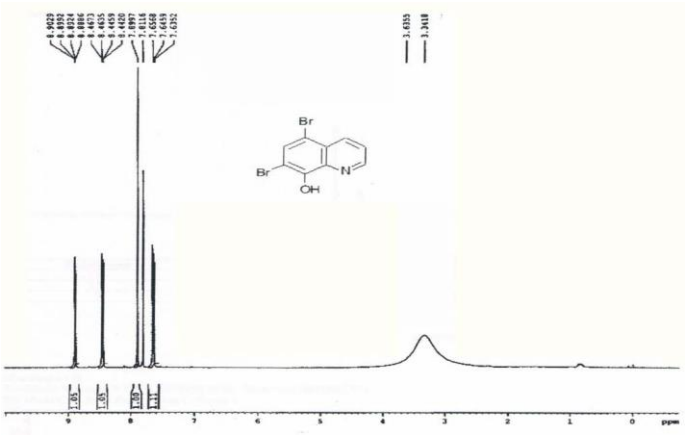


Fig. 7: 1H-NMR spectra of 5, 7-dibromooxine (**9**)

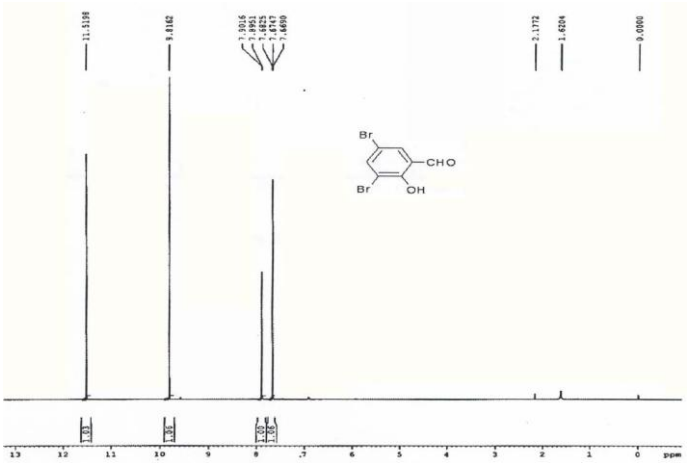


Fig. 8: 1H-NMR spectra of 3, 5-dibromosalicyladehyde (**10**)

methods, it progressed under exacting reaction conditions with poor end product yields.

RESULT AND DISCUSSION

Generally, all the halogens are highly reactive because of they have 7 electron in their outermost shell and as such can be hurtful or toxic to biological organisms in adequate volume or quantities. This high reactivity of halogens is due to low dissociation energy of their molecules. CetPyTB, having molecular formula $C_{21}H_{38}NBr_3$. The existence of Br_3^- was ascertained using the characteristic of tribromide. This is water decipherable reagent and polar solvents like acetonitrile, methanol and ethanol.

CetPyTB is hygroscopic in nature and needs to be warehoused in air tight containers. At this storage condition it gives long shelf life. The stability was determined by the determination of bromine contents periodically and rerecording of melting point from time to time. Cetylpyridiniumtribromide (CetPyTB), which is a pyridinium- based reagent (Chiappe et al., 2004; Kavala et al., 2005; Singhal et al., 2006), the focus on their methods of synthesis and their proficiencies in bromination. The active bromine content per molecule of cetylpyridiniumtribromide stayed found to be 44.01per cent as per elemental analysis. As the need to fetch in more and more reagents into the realm of newer reagents for organic transformations continues, there is a continuing effort to design and progress newer reagents. cetylpyridiniumtribromide (CetPyTB) have been synthesized in great yields by easy, environmentally gentle method with great yield result. All the ACS grade commercial chemicals were used without any further purification unless otherwise notified. Reactions were carried out in air with no precautions to exclude air or moisture. The reaction progress and completion were monitored by thin layer chromatography (TLC) by Silica G-60 UV254s glass plates from Merck, Germany.[7-8] The characterization of synthesized reagent was done by UV-vis and FT-IR were logged on a Bomen Hartmann and Braun MB series spectrometer. Melting points are uncorrected and are recorded in °C on Mettler Toledo FP62 device with open capillary tubes. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD spectrometer functioning at 500/200, and 125/50 MHz, respectively. The spectra were recorded in deuterated chloroform $CDC1_3$, CH_3DO and dimethyl sulfoxide as solvents unless otherwise noted. Chemical shifts are indicated in parts per million relative to Tetramethylsilane TMS, as an internal standard, for ^{1}H and ^{13}C NMR spectra. Common reagent grade chemicals were acquired from SD Fine Chemicals Ltd and also used without any further purification process (Fig. 3-10, Table 2). Wherever reflux condition mentioned, the reactions were executed in a two round long neck bottom hip flask equipped with reflux apparatus and reaction flask heated in oil bath at desired temperature on a magnetic stirrer which provides stirring and heating the reaction mixture.

Gas Chromatograph-Mass Spectrometry analysis done by Shimadzu GCMS-QP2010 Ultra. Restake Bellfonte‘s RTX- 5, low bleed, 60 m X 0.25 mm X 0.10 µm column was used for the analysis with a helium carrier gas flow of 1.2 mL /minute. The GC oven was held at 50°C for 3 minutes and then ramped at 20°C/minutes to 240°C where it was held for 10 minutes. A 0.5 µl injection with a 1:30 split was used throughout measurements. The absence of organic solvent in reaction process supported simple isolation procedure included separation of solid product and the aqueous liquid mixture thus accomplished containing

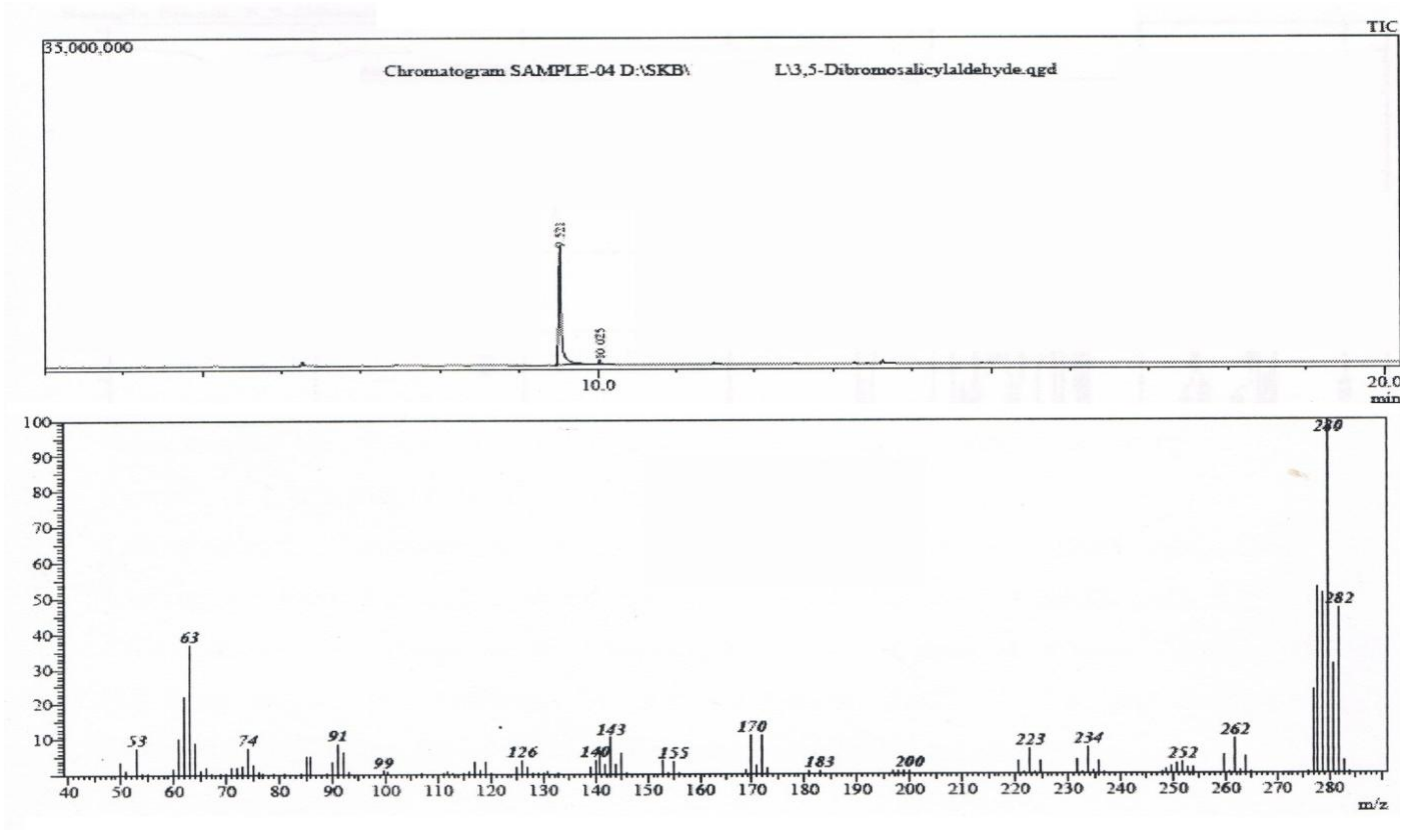


Fig. 9: GC-MS spectra of 3,5-dibromosalicyladehyde (**10**)

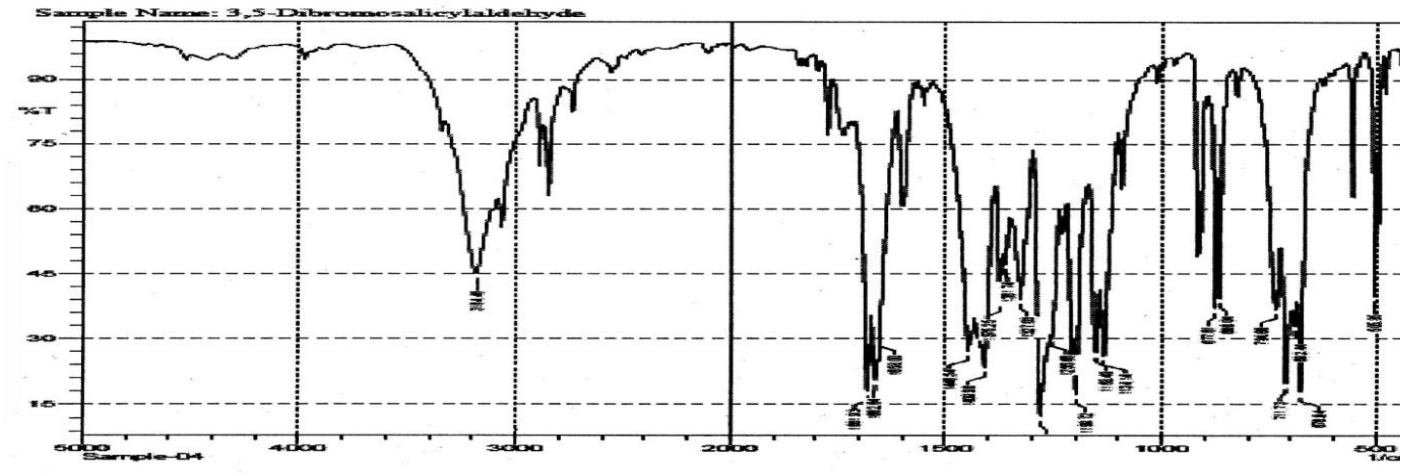


Fig. 10: IR spectra of 3, 5-dibromosalicyladehyde (**10**)

hydrogen bromide HBr, byproducts was neutralized by adding powdered calcium hydroxide $Ca(OH)_2$, As the present method shunned, the usage of any costly brominating agents, strong acids, hazards organic solvents, poisonous oxidants and metal catalysts, and functions completely in H_2O, it seemed valued to range this system for the bromination of other commercially-important organic compounds. Scale-up of the chemical reaction from laboratory to full sized commercial unit should not give any problematic issue for the micellar path because of the fast and facile bromination and quiet easy to handle workup procedure at both small and large scale.

CONCLUSION

In order to reduce the practice of toxic and high-cost organic solvents cast-off in traditional bromination methods/techniques, Cetylpyridinium Tribromide has been synthesized from a different route and its reactivity studied. It's easy method of preparation, gentleness and effectiveness in organic reactions

such as brominations put on view that the CetPyTB as a reagent could be a valuable count to the existing share of brominating reagents. This method was performed, purely in aqueous system which provides an eco-friendly reagent system for synthesis of organic brominated compounds with industrial importance in many sectors. A comparative study data of the brominating capability of the reported system with the of traditional reported approaches demonstrates that the present protocol is simple, faster, green, inexpensive, more reliable and proficient than the traditional catalytic bromination protocols used for this purpose. Spectral data (^{1}H NMR, Infrared and Mass Spectrometry) of brominated compounds is Specified as: ***4-bromoacetanilide (2)***: White powder; ^{1}H NMR (400 MHz, Dimethyl sulfoxide): δ 2.2 (3H, s), 7.28 (2H, d, J= 8.5 Hz), 7.47 (2H, d, J = 8.86 Hz), 9.89 (^{1}H, s); IR (KBr): 3142, 3130, 3128, 3111, 2989, 1658, 1632, 1598, 1578, 1544, 1460, 1386, 1314, 1276, 1237, 989, 863, 835, 722, 655, 517 cm-1; MS m/z calculated for C8H8BrNO: 217.08, FOUND 217. ***4-Bromobenzanilide (3)***: Light grayish powder; ^{1}H NMR (400 MHz, Deuterated Chloroform): δ 7.29-7.74 (9H, m); IR (KBr): 3348, 3033, 1675, 1549, 1406, 1178, 972, 866, 728, 704, 512 cm-1; MS m/z calculated for C13H10BrNO: 277.55, FOUND 277. ***2,4,6-Tribromoaniline (4)***: White-shiny needles; 1 H NMR (400 MHz, Deuterated Chloroform: δ 7.39 (s, ArH, 2H), 5.41 (bs, NH2, 2H); IR (Potassium Bromide): 3488, 3272, 1567, 1483, 1365, 1346, 1092, 844, 738, 711, 688, 563, 444 cm-1; MS m/z calculated for C6H4Br3N: 341.60, found 341. ***2,4-Dibromo-1-naphthol (6)***: Grayish-brown powder; ^{13}C NMR (100 MHz, Deuterated Chloroform): 150.10, 141.64, 132.74, 124.22, 121.90, 120.62, 118.92, 118.63, 108.32, 104.10; IR (Potassium Bromide): 3386, 3165, 2043, 1955, 1777, 1734, 1654, 1543, 1522, 1468, 1412, 1388, 1259, 1228, 1214, 1168, 1046, 1072, 954, 866, 848, 741, 721, 668, 653, 612, 578 cm-1; MS m/z (mass to charge ratio) calculated for C10H6Br2O: 310.22, found 310. ***1, 6-Dibromo-2-napthol (7)***: Light pinkish powder; ^{1}H NMR (400 MHz, Deuterated Chloroform): δ 6.32 (1 H, brs), 7.68-7.92 (2H, dd, J=77 and 9Hz), 8.22-8.36 (2H, dd, J =42 and 9 Hz), 8.68 (^{1}H, s); IR (Potassium Bromide): 3469, 3384, 1666, 1524, 1356, 1222, 1174, 932, 846, 811, 626, 548, 509 cm-1. ***5, 7-Dibromo-8-hydroxyquinoline (9)***: Light brown powder; ^{1}H NMR (400 MHz, Dimethyl Sulfoxide): δ 8.88 (dd, arom, ^{1}H), 8.54 (dd, arom, ^{1}H), 7.77 (s, 1H, arom) 7.59 (t, ^{1}H, arom); IR (Potassium Bromide): 3186, 1845, 1644, 1636, 1559, 1472, 1466, 1386, 1324, 1315, 1265, 1167, 1081, 942, 926, 838, 816, 752, 755, 674, 569, 510 cm-1 ; MS m/z (mass to charge ratio) calculated for C9H5Br2NO: 303.88, found 303. ***3, 5-Dibromosalicylaldehyde (10):*** Light yellow powder; ^{1}H NMR (400 MHz, Deuterated Chloroform): δ 7.84 (d, ^{1}H, J=2.25 Hz, ArH), 7.88 (d, ^{1}H, J=2.58 Hz, ArH), 9.78 (S, COOH, ^{1}H), 11.76 (s, OH, ^{1}H); IR (Potassium Bromide): 3278, 1786, 1765, 1666, 1537, 1514, 1474, 1426, 1385, 1357, 1285, 1223, 1208, 1192, 976, 858, 822, 792, 747, 699, 512 cm-1; MS m/z (mass to charge ratio) calculated for C7H4Br2O2: 280.8 found 281. ***2, 6-Dibromo-4-nitroaniline (18)***: Yellow powder; ^{1}H NMR (400 MHz, Dimethyl Sulfoxide): δ 8.46 (2h, s), 6.92 (^{1}H, s); IR (Potassium Bromide): 3580, 3426, 3054, 2973, 2674, 2382, 1964, 1828, 1792, 1655, 1585, 1468, 1361, 1243, 1167, 1025, 968, 882, 766, 624, 475 cm-1; MS m/z (mass to charge ratio) calculated for C6H4Br2N2O2: 292.8, found 292.

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