A Novel Metal- and Mineral-acid free Synthesis of Organic Ammonium Tribromides and Application of Ethylenephenanthrolium Bistribromide for Bromination of Active Methylene Group of 1, 3-Diketones and *β*-Ketoesters

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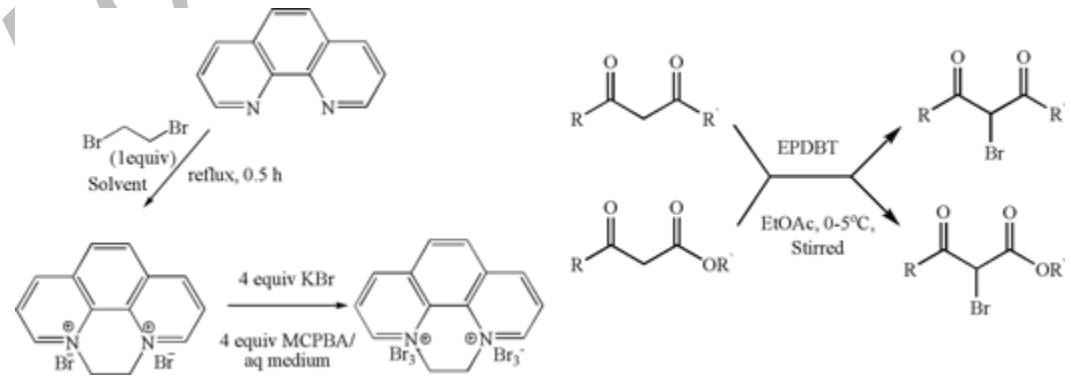
Abstract

A novel procedure for the preparation of organic ammonium tribromides (OATBs) is described from their corresponding bromides. Quaternary ammonium bromides (QABs) and a N, N′-heterocyclic dibromide are efficiently oxidized to their corresponding mono-tribromides and bistribromide by *m*-chloroperbenzoic acid (MCPBA) in presence of 2 and 4 equiv of KBr, respectively. The reactions are carried out in aq. medium without the use of any mineral acid and metal catalyst/promoters. A variety of tribromides are synthesized in very high yields including a hitherto unknown reagent *viz.* 1, 10-(ethane-1, 2-diyl)phenanthrolinediium bistribromide (EPDBT). EPDBT is investigated as brominating agent and found to be highly effective for selective bromination of active methylene groups of a variety of 1, 3-diketones and *β*-ketoesters.



KEYWORDS: MCPBA, bistribromide, bromination, 1,3-diketones, β-ketoesters, metal-free

INTRODUCTION

Over the past two decades or so, sustainable and eco-friendly organic preparations have attracted huge attention of synthetic organic chemists across the globe due to environmental issues with most of the traditional synthetic methodologies.[1] A few components that contribute heavily towards environmentally clean reactions are solvent-free or aq medium reactions, use of non-toxic reagents, obtaining higher yields in lesser time *etc*.[2] In recent past, Quaternary Ammonium Tribromides (QATBs) and N-Heterocyclic Ammonium Tribromides (NHATBs) have garnered significant interest owing to their versatile utility in synthetic organic chemistry.[3] Conventionally, QATBs and NHATBs are prepared using potentially dangerous liquid Br_2 and/or HBr and thus considered to be not favorable from environmental perspective.[4] Over the past few years, many improved methods of synthesis of OATBs were reported that involve oxidation of Br^- to Br_3^- in efficient and environmentally benign manner. A few of them worth mentioning are V_2O_5/H_2O_2,[5] $MoO_4^{2-}/H_2O_2/H^+$,[5] MnO_4^-/H^+,[6] $(NH_4)_2S_2O_8/H^+$,[7] $NaOCl/H^+$,[8] H_5IO_6,[9] oxone[10] *etc*. In spite of several advantages, many of such methods usually involve metals and mineral acids which still cause environmental concerns. Therefore, development of newer methods which can do away with metals and mineral acids is still a challenge for synthetic chemists. Organic oxidants are often considered superior to inorganic ones because of their mildness and efficacy. Moreover, on many occasions they don't require any mineral acids to carry out the oxidative transformations.

Some organic oxidants like DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone), *t*-BuOOH, MCPBA in particular, is highly useful oxidant in organic syntheses as it possesses several advantages such as cheap, non-hazardous, highly efficient and often requires no catalyst to generate products in high yields. An exhaustive literature survey reveals that MCPBA has never been used in the conversion of Br^- to Br_3^- leading to the synthesis of tribromide reagents. Among the tribromides, QATBs are reported to be more useful as reagents or catalysts in a variety of organic reactions. Relatively less is known about N-heterocyclic tribromides, especially N, N′ -heterocyclic bistribromides. Recently, Patel *et al.* have prepared 1, 1´-(ethane-1, 2-diyl)dipyridinium bistribromide as stable bistribromide by using oxone.[10] The compound is found to have vast utility in organic reactions like bromination of organic substrates (alkene, alcohols and amines) and synthesis of heterocyclic compounds.[11] A few more bistribromides particularly DABCO-Bromine[12] and ethylenebis(N-methylimidazolium)ditribromide[13] are known in the literature, which also have high utilities as reagents in organic synthesis.

In the context of application of tribromides as brominating agent, attention may be drawn to the importance of regio-selective bromination of 1, 3-dicarbonyls and *β*-ketoesters at *α*-position due to their versatility as intermediates in organic synthesis.[14] Such brominated products often serve as useful building blocks in the synthesis of natural and non-natural products.[15] Most commonly used reagents to access those monobrominated products include Br_2,[16] H_2O_2-HBr,[17] NBS,[18] $CuBr_2$-Koser's reagent,[14a] NaOBr in acetone/AcOH,[19] NH_4Br-oxone,[20] bromodimethylsulfonium bromide[21] (BDMS) *etc*. Though, these methodologies generate good yield of products, but most of them suffer

from drawbacks such as harsh reaction conditions, difficult work-up technique *etc*. Moreover, selectivity is an issue with some of these methodologies which lead to dibrominated products as well.[14a,22]

In the backdrop of discussion made above on the importance of tribromides and their applications, it becomes evident that developing newer methodologies for such reagents that are efficient and environmentally acceptable, would still pose a challenge to synthetic organic chemists. As a part of our constant endeavor[6–9] over the past couple years to develop newer synthetic strategies for tribromide reagents and their applications, we would like to report herein, a new procedure for synthesis of tribromides that include a variety of QATBs, *viz* tetramethylammonium tribromide (TMATB), tetraethylammonium tribromide (TEATB), tetrabutylammonium tribromide (TBATB), cetyltrimethylammonium tribromide (CTMATB) and benzyltrimethylammonium tribromide (BTMATB) and a N, N -heterocyclic bistribromide. The bistribromide, *viz*. 1, 10-(ethane-1, 2-diyl)phenanthrolinediium bistribromide (EPDBT) is hitherto unknown and thus it makes new addition to the family of tribromide reagents. With the successful synthesis of EPDBT as new reagent, it is considered a worthwhile task to explore the efficacy of this reagent in α-bromination of 1, 3-dicarbonyls and β-ketoesters.

RESULTS AND DISCUSSION

All the QATBs have been prepared very efficiently by carrying out oxidation of Br^- to Br_3^- by using MCPBA as oxidizing agent. A variety of tribromides, tetramethylammonium tribromide (TMATB), tetraethylammonium tribromide (TEATB),

tetrabutylammonium tribromide (TBATB), cetyltrimethylammonium tribromide (CTMATB) and benzyltrimethylammonium tribromide (BTMATB) have been prepared by mixing corresponding bromide with 2 equiv KBr and oxidizing the whole with MCPBA (Scheme **1**). The resulting QATBs have been obtained in nearly quantitative yields.

Similar methodology has been adopted to prepare EPDBT (Scheme 2). The first step involves conversion of 1, 10-phenanthroline into a dibromide intermediate (1,10-ethane-1,2-diyl phenanthrolinediium dibromide) by the literature method.[23] The dibromide thus formed was isolated and characterized by spectroscopic techniques. Four equiv of oxidant (MCPBA) and 4 equiv KBr have been added to the intermediate to convert it to its corresponding bistribromide. Excess of MCPBA, if any, was destroyed by treating the reaction mixture with aq solution of 10% $NaHCO_3$ which, subsequently, converts remaining MCPBA to sodium chlorobenzoate, H_2O and CO_2. The tribromides were finally extracted with minimum volume of EtOAc. Removal of solvent afforded the pure product. It should be pointed out that H_2O_2 or molecular oxygen are perhaps more environmentally friendly than MCPBA but our experience and survey of literature reveal that such oxidants alone cannot effectively carry out transformation of Br^- to Br_3^-. They often require transition metals as activator[5b] and/ or mineral acid such as H_2SO_4. The use of transition metals in stoichiometric amount or mineral acid in a reasonable concentration may pose environmental issues in spite of highly friendly character of molecular O_2 or H_2O_2. MCPBA has its inherent acidity and very effective in oxidizing

Br^- to Br_3^- without a metal activator which is why the present methodology is believed to be environmentally safe.

All the QATBs and EPDBT were characterized by UV-Visible, FT-IR, ^1H and ^{13}C NMR spectroscopy. The QATBs are all known compounds and their analytical data consistent with literature reports. A intense band appeared at 269 nm in the UV-Vis spectrum (Figure **1**) for EPDBT is characteristic for tribromide ion (Br_3^-).[5a] The FT-IR spectra of the compound (Figure **2)** shows characteristic peak at 196 cm^{-1} indicating the presence of Br_3^- moieties in the compound.[24] In the ^1H NMR spectrum of EPDBT, it can be observed that the peak at δ value 2.20 is certainly for the ethylene protons attached to the N-atoms. However no such peak may be observed in the ^1H NMR spectrum of phenanthroline.

After getting pure EPDBT, we performed the bromination reaction taking methyl acetoacetate (**1a**) as model substrate. Ethyl acetate was found to be the suitable solvent for the bromination of β-carbonyl compounds. Initially, 0.6 mmol of EPDBT was dissolved in ~ 5 mL of EtOAc followed by the addition of **1a**. The reaction mixture was stirred for several min in a magnetic stirrer maintaining ice-cold condition. TLC was run to monitor the reaction (10% EtOAc/hexane). It took ~ 25 min to complete the reaction with 96% yield. No trace of dibrominated product was detected even with excess of EPDBT. After getting success with **1a**, we tried α-monobromination of some selectively chosen 1, 3-diketone and β-ketoester substrates (**2a**-**14a**). All of these substrates were brominated by pursuing similar reaction condition mentioned for **1a** affording products in

80-96% and in a short reaction time, (Table **1**). In most of the cases, the predicted *α*-monobrominated product was formed. But in case of some particular substrates likely, **5a**-**7a**, **9a**, **13a**-**14a**, a trace amount of ring bromination was also observed. It may be added that, according to literature survey,[25] bromination is also possible at the C-1 position of 1, 3-diketones *viz.* **3a**, **5a** or **11a**. However, no such bromination was observed at that position as EPDBT as brominating agent. It is apparent from table **1** that *ß*-ketoesters requires relatively longer time as compared to 1, 3-diketones which can be explained in terms of the P_{ka} value of $–CH_2–$ protons. For example, yield of **2b** is 89 % in ~ 24 min which is higher than that of **3b** for similar reaction condition. It may be further mentioned that the bromination was also tried taking other solvents like CH_2Cl_2 and MeCN which led to good yield of products. But those solvents were avoided because of environmental issues.[26] Scheme **3** shows the bromination of diketone and *β*-ketoesters by EPDBT.

A plausible mechanism of 1, 3-diketone bromination by tribromide may be explained by scheme **4**. Initially diketone undergoes tautomerism and transform itself to enol-form. In the next step, the bromine molecule generated from EPDBT extracts the acidic proton from enolated diketone as HBr giving the desired product.

CONCLUSION

In conclusion, we have come up with a novel synthetic protocol for the synthesis of organic ammonium tribromides and a N, N-heterocyclic bistribromide, EPDBT, employing m-chloroperbenzoic acid as oxidant for transformation of Br^- to Br_3^-. EPDBT

has been added as a new tribromide reagent to the host of already existing tribromide based compounds. Although quite a few environmentally benign methods for synthesis of tribromides are known in the literature, the new procedure reported herein will certainly be one of the effective tools for accessing such reagents. This new tribromide is found to be a reagent of choice for selective bromination of active methylene group of diketones and ketoesters leading to nearly quantitative yield of α-monobrominated products. The notable advantage of this method is mildness, region-selectivity and very good yields. Moreover, the process requires no bases or lewis acid or other catalyst to get products. The methodology has the potential to make a value addition to the existing protocols for monobromination of diketones and ketoesters.

EXPERIMENTAL

General Procedure For The Synthesis Of Qatbs By MCPBA

The general procedure involves the mixing of 1 equiv of quaternary ammonium bromide (1 mmol), 2 equiv of KBr (2 mmol, 0.238 g) and 2 equiv of MCPBA (2 mmol, 0.346 g) in 10 mL of water and stirring of reaction mixture for several min. An orange coloured product formed was washed with $NaHCO_3$ solution (10 % solution) for several times to remove unreacted substrate. After that the crude product was again washed with water to remove by-products. After that the crude product was again washed with water to remove by-products and extracted with EtOAc. Removal of solvent afforded the pure product.

Synthesis Of EPDBT By MCPBA And Its Characterization

Firstly, 1,10-(ethane-1,2-diyl)phenanthrolinediium dibromide was prepared by refluxing phenanthroline (10 mmol, 1.96 g) and 1,2-dibromoethane (10 mmol, 1 mL) in acetone (6 mL) in a round bottom flask for 0.5 h at temperature of 90^{o}C. The solid product of dibromide precipitated was filtered, followed by washing with Et_2O (2 X 10 mL), dried in vacuum and then recrystallized from EtOH-water (2:5) mixture.

Now 1 equiv of dibromide, thus synthesized (1 mmol, 0.354 g), 4 equiv of KBr (4 mmol, 0.476 g) and 4 equiv of MCPBA (4 mmol, 0.692 g) were mixed in 10 mL of water and stirred for *ca*. 5 min. The orange coloured product formed was washed with $NaHCO_3$ solution (10 %) for several times to remove unreacted MCPBA. After that the crude product was again washed with water to remove by-products and extracted with EtOAc. Removal of solvent afforded the pure product.

EPDBT: Orange compd; mp 97^{o}C; Yield: 90 % (0.610 g); UV-Vis: 269 nm; FT-IR (KBr, cm^{-1}): 3383, 2968, 1466, 779, 196; ^{1}H NMR δ: 9.18 (t, J = 1.8 Hz, 2H), 8.24-8.22 (t, J = 2.8 Hz, 2H), 7.77-7.57 (dd, J = 3.5 Hz, $J^{`}$ = 1.5 Hz, 2H), 7.62 (s, 2H), 2.20-1.96 (m, 4H); ^{13}C NMR δ: 77, 123, 126, 129, 136, 146, 150; Anal., $C_{14}H_{12}N_2Br_6$ (Mol Wt 687.66): Calcd C 24.45, H 1.76, N 4.07, Br 69.71; Found C 24.60, H 1.69, N 3.99, Br 69.65.

Bromination Of 1, 3-Diketones And B-Ketoesters By EPDBT With Spectral And Analytical Data Of Some Products

0.6 mmol of EPDTB (0.818 g) was dissolved in 5 mL of EtOAc followed by the addition of 1 mmol of 1, 3-diketone/β-ketoester to the reaction mixture. The above mixture was

stirred maintaining cool condition (5-10^{o}C) in a magnetic stirrer for several minutes until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na_2SO_4 after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude product.

Methyl 2-bromo-3-oxobutanoate (1b): Oily liquid; bp 215^{o}C; Yield: 96 %; FT-IR: 3493, 2986, 1792, 1718, 869 cm^{-1}; ^{1}H NMR δ: 4.19 (s, 1H), 3.07 (s, 3H), 2.18 (s, 3H); ^{13}C NMR δ: 27, 51, 67, 164, 201; Anal., $C_5H_7O_3Br$ (Mol Wt 195.01): Calcd C 30.79, H 3.62; Found C 30.73, H 3.58.

Ethyl 2-bromo-3-oxobutanoate (2b): Liquid; bp 230-232^{o}C; Yield: 89 %; FT-IR: 1745, 1718 cm^{-1}; ^{1}H NMR δ: 4.70 (s, 1H), 3.38 (q, J = 7.1 Hz, 2H), 2.45 (t, J = 7.1 Hz, 3H), 1.27 (s, 3H); ^{13}C NMR δ: 15, 26.3, 55, 67, 163, 198; Anal., $C_6H_9O_3Br$ (Mol Wt 209.03): Calcd C 34.47, H 4.34; Found C 34.50, H 4.37.

3-Bromopentane-2,4-dione (3b): Liquid; Yield: 88 %; FT-IR: 1743, 1721 cm^{-1}; ^{1}H NMR δ: 4.17 (s, 6H), 2.07 (s, 1H); ^{13}C NMR δ: 27, 67, 195; Anal., $C_5H_7O_2Br$ (Mol Wt 179.01): Calcd C 33.52, H 3.94; Found C 33.47, H 3.90.

***t*-Butyl 2-Bromo-3-oxobutanoate (4b)**: Liquid; bp 240^{o}C; Yield: 92 %; FT-IR: 1732, 1718 cm^{-1}; ^{1}H NMR δ: 4.10 (s, 1H), 2.02 (s, 3H), 1.23 (s, 9H); ^{13}C NMR δ: 27, 31, 67,

84, 164, 206; Anal., $C_8H_{13}O_3Br$ (Mol Wt 237.09): Calcd C 40.53, H 5.53; Found C 40.41, H 5.57.

SUPPORTING INFORMATION

Supplemental data for this article can be accessed on the publisher's website.

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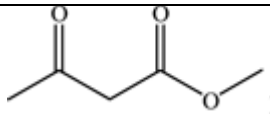
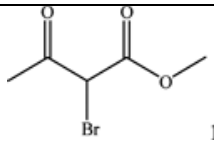
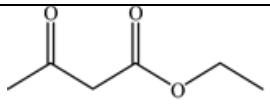
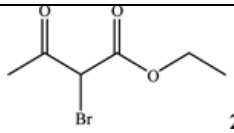
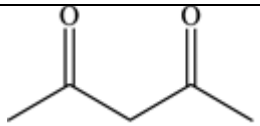
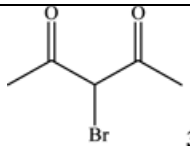
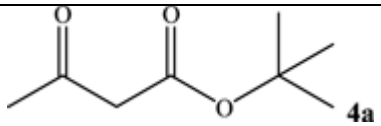
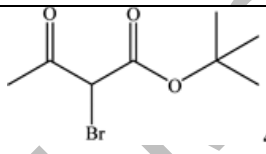
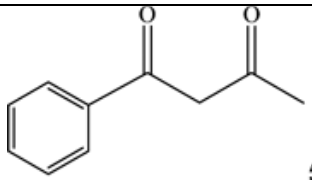
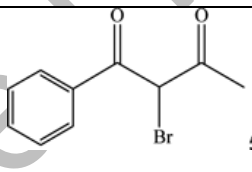
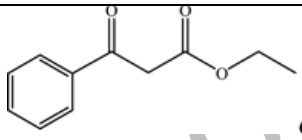
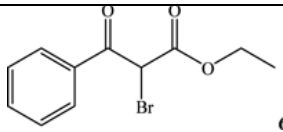
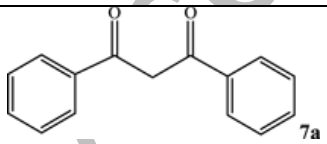
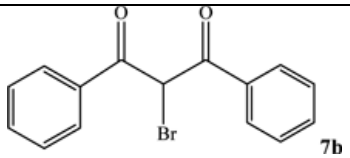
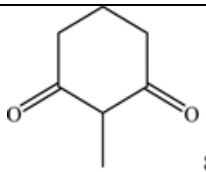
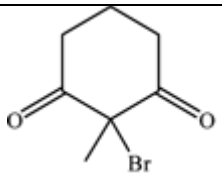
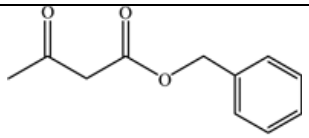
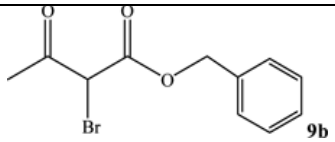
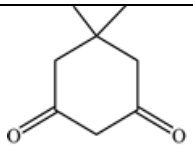
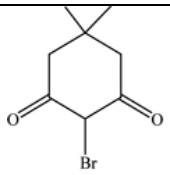
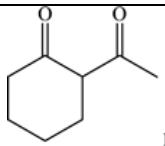
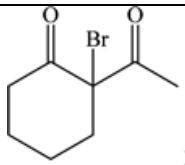
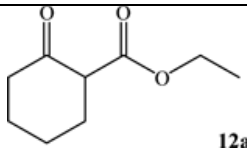
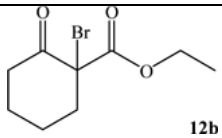
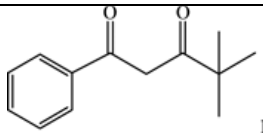
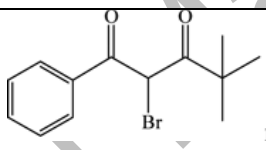
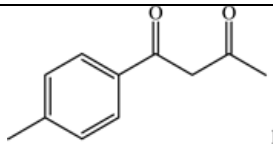
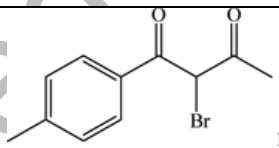
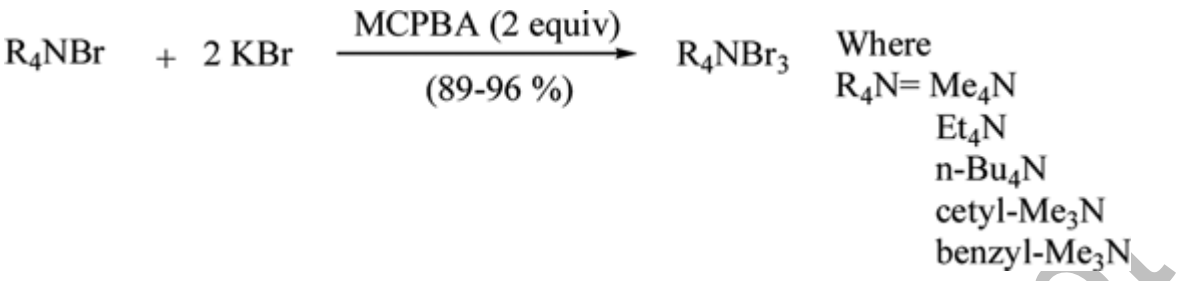
Table 1. Monobromination of 1, 3-diketones and *β*-ketoesters by EPDBT

Entry	Reactants	Products	Reaction Time (Min)	Yield	Ref.
1	 **1a**	 **1b**	25	96	27
2	 **2a**	 **2b**	25	89	21(a)
3	 **3a**	 **3b**	20	88	13
4	 **4a**	 **4b**	30	92	10
5	 **5a**	 **5b**	15	80	25
6	 **6a**	 **6b**	30	82	18
7	 **7a**	 **7b**	15	85	17
8	 **8a**	 **8b**	20	86	18

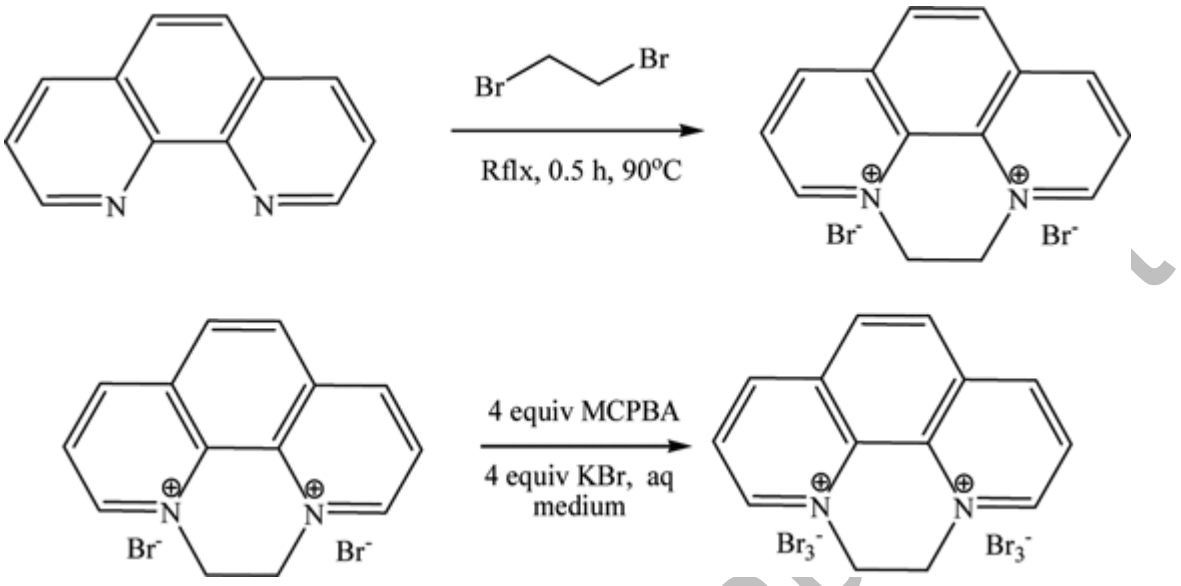
9	 **9a**	 **9b**	30	92	10
10	 **10a**	 **10b**	20	80	10
11	 **11a**	 **11b**	20	81	18
12	 **12a**	 **12b**	25	85	28
13	 **13a**	 **13b**	15	81	-
14	 **14a**	 **14b**	15	80	-

[a]The reaction was conducted in temp 5-10^{o}C using reagent to substrate molar ratio 1:0.6 and taking EtOAc as the solvent. [b]All the products were first checked in TLC and then identified by FT-IR and NMR spectral data. [c]Isolated Yield.

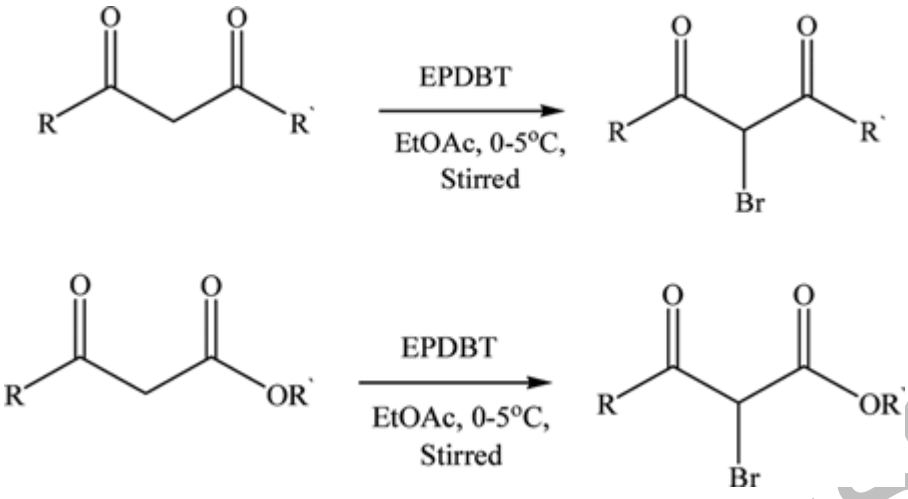
Scheme 1. Reaction showing the synthesis of QATBs from QABs by MCPBA**.**



Scheme 2. Strategy for the preparation of EPDBT.



Scheme 3. Bromination of 1,3-diketones and β-ketoesters by EPDBT.



Scheme 4. A plausible mechanism for the bromination of 1, 3-diketones.

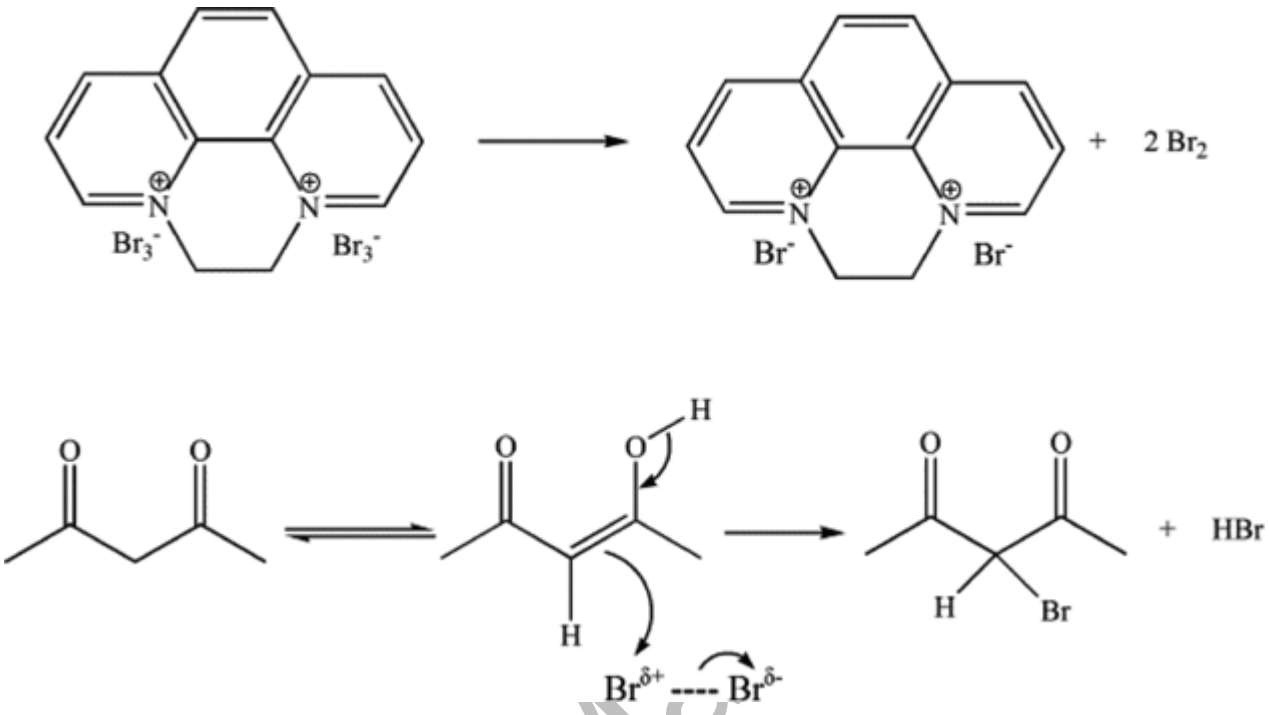


Figure 1. UV-Visible Spectra of EPDBT

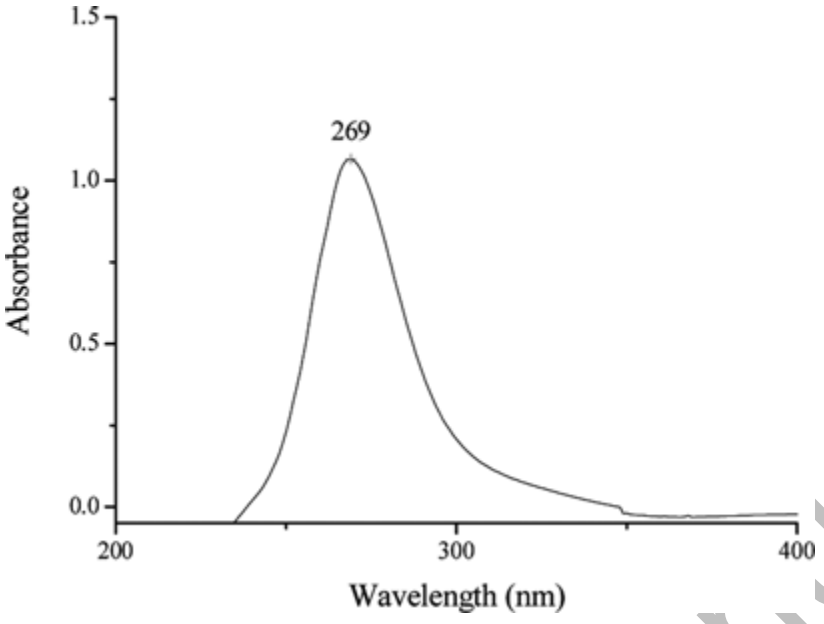


Figure 2. FT-IR spectra of EPDBT