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A recyclable PEG-crowned potassium tribromide $[\{K^+PEG\} \cdot Br_3^-]$ for the synthesis of tetrabromobisphenol A

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Abstract

Polyethylene glycol-bound potassium tribromide $[\{K^+PEG\} \cdot Br_3^-]$ was found to be an efficient brominating agent for the bromination of bisphenol A to tetrabromobisphenol A of a very high purity in excellent yield. The brominating agent was easily prepared by reacting the PEG₄₀₀ with KBr₃ using the host-guest chemistry concept. The effect of various reaction parameters such as solvent, temperature, and concentration of brominating agent on the yield and purity of tetrabromobisphenol A was studied. The key advantages of the developed method are the use of inexpensive, non-volatile poly(ethylene)glycols, facile regeneration, and inbuilt recycling of generated HBr waste.

Keywords: Bromination, Bisphenol A, Tetrabromobisphenol A, PEG, Recyclable reagent

Background

The formation of host-guest complexes between crown ethers and alkali metal cations is well known and is being used worldwide in various fields such as supramolecular chemistry, biomimetic chemistry, and materials science [1]. However, the expensive nature and limited accessibility of the crown ethers make their utility limited. Compared with the crown ethers, poly(ethylene) glycols (PEGs) have many advantages such as having a much lower cost; being nontoxic, biodegradable, and easily accessible; and displaying complexation properties which are similar to crown ethers [2,3]. Therefore, PEGs are known as a 'poor chemist's crown ethers' and can successfully replace crown ethers for various applications [4,5]. These advantageous features inspired us to use PEGs in the formation of host-guest type complexes for industrially important chemical reactions.

Tetrabromobisphenol A (TBBPA) with the chemical name 4,4'-isopropylidene-bis-(2,6-dibromophenol) is a versatile chemical which has been used worldwide in the preparation of brominated flame retardants in electronic appliances, automotives, textiles, and furniture industries [6,7]. It is also used to provide flame retardancy for styrenic thermoplastics and for some thermoset resins.

Conventionally, the synthesis of TBBPA involves the direct bromination of bisphenol (BPA) with molecular bromine in methanol [8]. This method suffers from many drawbacks such as the cumbersome handling of liquid bromine and the generation of the substantial amounts of methyl bromide as by-product.

Consequently, some improved methods for the bromination of bisphenol at a low temperature, e.g., 0°C to 20°C, using methanol/water mixture have been developed [9-11] since the presence of water and low temperature attenuates the production of methyl bromide and therefore overcomes the limitations of the conventional bromination method. However, the longer reaction times and requirement of additional steps for the final precipitation of tetrabromobisphenol A are the major drawbacks associated with these methods.

Recently, the use of organic ammonium tribromides, molecular bromine in conjunction with oxidants, and HBr-H₂O₂ has been reported to be efficient for the bromination of bisphenol A [12,13]. Despite their potential applicability, most of the methods have some limitations such as high cost, difficult handling, longer reaction times, and, moreover, less purity of the desired product. Very recently Kumar et al [14] reported that potassium tribromide (KBr₃) as a highly efficient brominating agent provided instantaneous bromination of bisphenol to TBBPA. This method is advantageous in many ways

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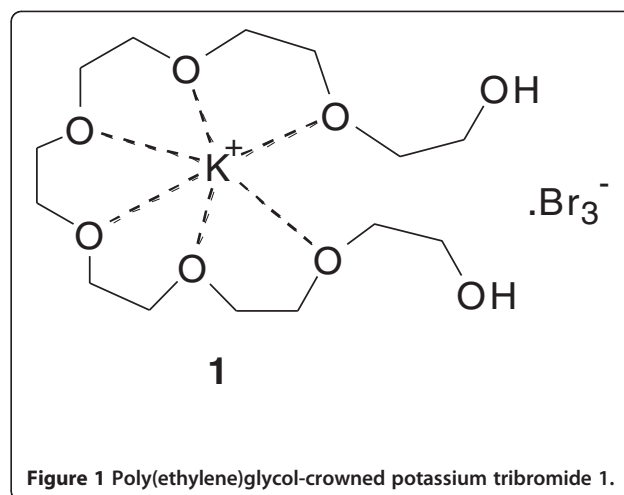
as it describes the inbuilt recycling of generated HBr, cost-effective nature of the brominating agent, and high purity of the desired product. However, difficult solvent recovery and neutralization of the alkali metal halide prior to the recycling of brominating agent make the utility of this method limited. Therefore, the development of an efficient, recyclable, and cost-effective brominating agent for the bromination of TBA is still required. With continuous interest towards developing novel synthetic methodologies for organic reactions, herein, we report for the first time a highly efficient, readily synthesized, and recyclable brominating agent, i.e., poly(ethylene)glycol-crowned potassium tribromide $[[K^+PEG]\cdot Br_3^-]$ **1** (Figure 1) for the bromination of BPA to TBBPA.

Methods

The melting points were determined in open capillaries on a Buchi apparatus and are uncorrected. The 1H NMR Spectra were recorded on Bruker 300 MHz spectrometer and the chemical shifts are expressed in δ parts per million relative to tetramethylsilane (TMS) as internal standard. The IR spectra were recorded on a Perkin Elmer FTIR X 1760 instrument. Elemental analysis was done by using ASTM D-3828 (Kjeldhal method). HPLC analyses were conducted using a Waters 2695 instrument, Meadow Instrumentation with PDA detector using solvent system (70% CH_3CN + 30% H_2O), and a flow rate of 1 ml/min.

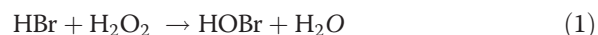
Result and discussion

The required PEG-bound tribromide reagent **1** could readily be synthesized by following the published procedure [15]. The loading of the reagent was found to be 1.2 mmol/g as determined by elemental analysis. The corresponding brominating agents of PEG₂₀₀ and PEG₆₀₀ were formed successfully, albeit the solid PEG, i.e., PEG₂₀₀₀, gave a sticky material which was difficult in handling; thus, we used compound **1** for further studies. The prepared reagent was dark red in color which disappeared during the bromination of BPA. After completion of the reaction, no bromine could be detected in the reaction mixture as analyzed by UV-Vis spectroscopy; this established the *in situ* generation of bromine from the reagent during the reaction. The bromination of BPA with tribromide **1** was performed at 25°C using water as a reaction media

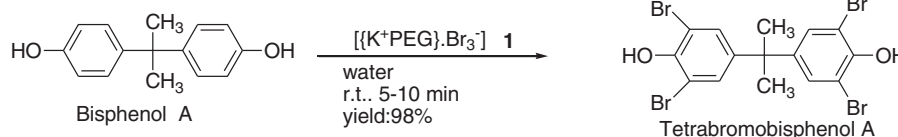


(Scheme 1). The progress of reaction was monitored by thin layer chromatography (TLC). After isolating the brominated product from the reaction mixture, the aqueous layer was treated with bromine in a controlled manner to regenerate the brominating reagent **1**.

The regenerated reagent could easily be recovered from the aqueous layer by extraction with dichloromethane. The combined organic layer was under reduced pressure; the viscous oil was dried under vacuum and reused for next run. The remaining aqueous layer containing HBr waste could be used for the bromination using H_2O_2 , resulting in the formation of activated brominating species *in situ*, i.e., hypobromous acid (HOBr) according to the following equation [16]:



In order to establish the utility and versatility of the present method, we also studied the effect of various reaction parameters to the yield and purity of the desired product. To evaluate the effect of the solvent, bromination of bisphenol was carried out with **1** in different solvents under identical reaction conditions. The results of these experiments are plotted in Figure 2. The purity of the product could easily be analyzed by the high-performance liquid chromatography (HPLC) analysis. As depicted in Figure 2, water was found to be the best reaction medium in the bromination of bisphenol



Scheme 1 Bromination of bisphenol A.

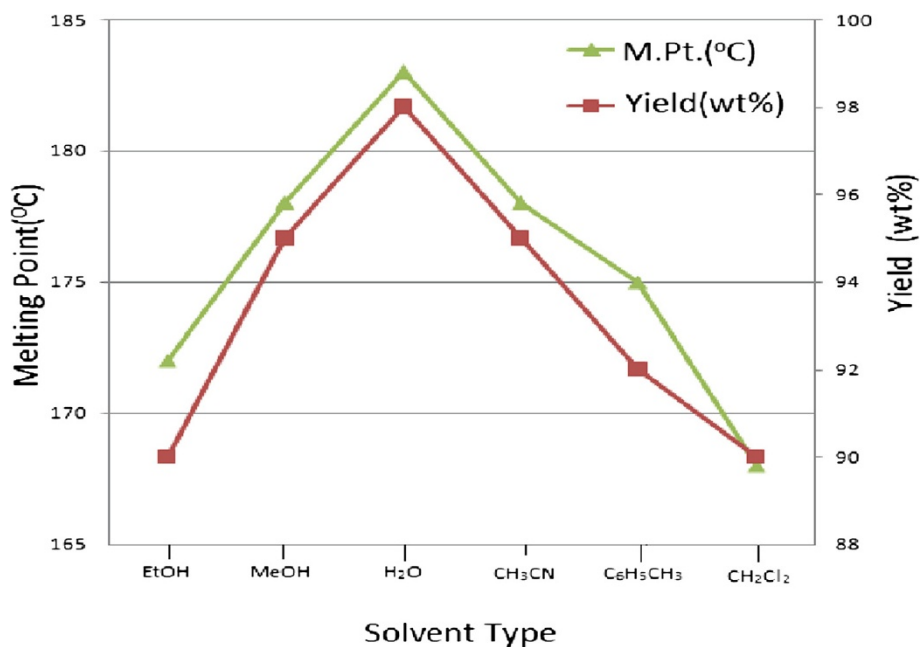


Figure 2 Effect of solvent on the yield and melting point of TBBPA.

A to TBBPA in terms of yield (98%), melting point (M.Pt.) (182°C), and color (white crystalline solid), making the method advantageous from environmental viewpoints. Other solvents such as methanol, ethanol, acetonitrile, toluene, and dichloromethane were also found to be less effective and afforded poor product yield, suggesting the presence of an under-brominated product. The presence of water enhanced the rate of

reaction, probably due to the conversion of hydrogen bromide to hydrobromic acid, which allows thorough bromination of bisphenol A, which otherwise was inhibited by the presence of HBr. Another reason for the significant acceleration in water is due to the formation of hypobromous acid in the system ($\text{Br}_2 + \text{H}_2\text{O} = \text{HOBr} + \text{HBr}$), which serves to be the active brominating species.

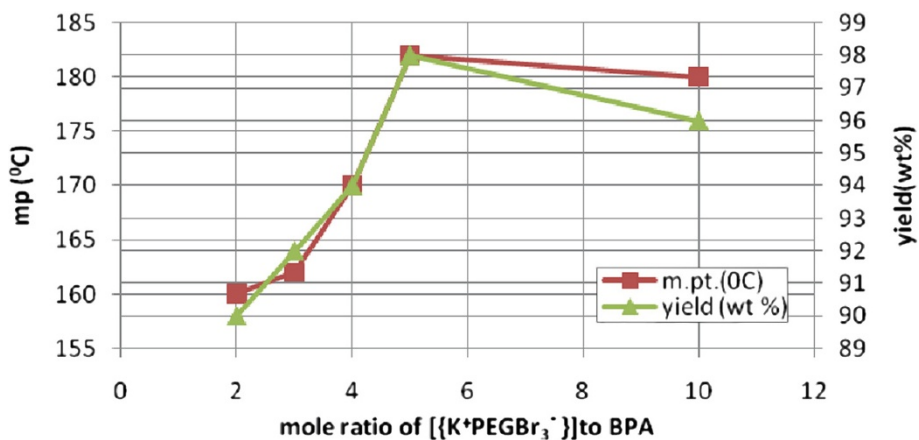


Figure 3 Effect of mole ratio of 1/BPA on the yield and melting point of TBBPA.

Similarly, we studied the bromination of BPA by changing the mole ratio of **1** to BPA from 2:1 to 10:1 under similar reaction conditions. As shown in the Figure 3, the quality of the product is strongly dependent on the mole ratio of **1**/BPA. It has been observed that the optimum yield of TBBPA (98%) with desired purity (99.2% as analyzed by HPLC) was obtained when the mole ratio of **1**/BPA was 5.0/1, whereas, the lower concentration of **1** afforded the brominated product of less purity, probably due to the formation of under-brominated products. The purity of the product was found to be increased as the mole ratio was increased from 2 to 5 mol%; however, a further increase in the mole ratio of **1** affected the quality as well as yield of the product adversely, and we could get less yield of the desired product with decreased purity.

The effect of reaction temperature was studied by performing the bromination of BPA at different temperatures varying from 15°C to 75°C. The results of these experiments are summarized in Table 1. At the lower reaction temperature (15°C), the yield and purity of the product remained comparable albeit the reaction required a longer reaction time (30 to 60 min) in completion. However, 25°C to 30°C was found to be the optimum temperature for this reaction and afforded excellent product yield with high HPLC purity. The lower reaction temperature is another advantage, which further makes this method superior over the existing ones, which employed temperatures >55°C.

Next, we checked the regeneration and recycling of the brominating agent. At the end of the reaction, the brominated product TBBPA was isolated by simple filtration and dried under reduced pressure. The M.Pt. of the white crystalline powder of TBBPA was found to be sharp (182°C) with the 99.2% purity (as analyzed by HPLC). The filtrate so obtained containing {PEG-KBr} and HBr was treated with bromine in a controlled manner to regenerate the reagent **1**. The dark colored reagent **1** was recovered from the aqueous solution by extraction with dichloromethane, dried under vacuum, and reused for the subsequent run. Also, the remaining aqueous layer containing HBr was treated with aqueous H₂O₂ to generate *in situ* HOBr and used for the

Table 1 Effect of reaction temperature

Entry	Temperature (°C)	Yield (%)	Purity of TBBPA (%) ^a
1	15	97.5	98.6
2	25	98	99.2
3	30	97	99.0
4	40	98	94.0
5	50	98	85.0
6	75	97	80.0

Reaction temperature conditions: BPA (1mmol), **1** (5 mmol), and water (2 ml);
^apurity was analyzed by HPLC.

Table 2 Results of recycling experiments

Parameters of TBBPA	Run 1	Run 2	Run 3	Run 4	Run 5
M.Pt. (°C)	182	183	181	182	182
Yield (%) ^a	98	97.5	97.5	98	97
Purity (%) ^b	99.2	99.3	99.2	99.2	99.2

Experiment conditions: BPA (1 mmol), reagent **1** (5 mmol), and water (5 ml) at 25°C; ^aisolated yield of TBBPA; ^bpurity of the product was analyzed by HPLC.

bromination of bisphenol A. The results of recycling experiments are summarized in Table 2. As shown, the yield, melting point, and purity of the obtained TBBPA during the recycling experiments were found to be almost the same, establishing the successful regeneration, recycling of **1**, and inbuilt utilization of HBr for the bromination of BPA to TBBPA.

The exact mechanism of this reaction is not clear at this stage; however, we could assume that the reaction probably involves the *in situ* generation of bromine from [{K⁺PEG}-Br₃], which reacts with water to give HOBr **2**. The electrophilic addition of Br⁺ to BPA yields TBBPA along with the formation of 4 mol of HBr as by-product. The generated HBr could easily be recycled by treating with H₂O₂ to give *in situ* HOBr, which subsequently reacts with BPA to afford TBBPA (Scheme 2).

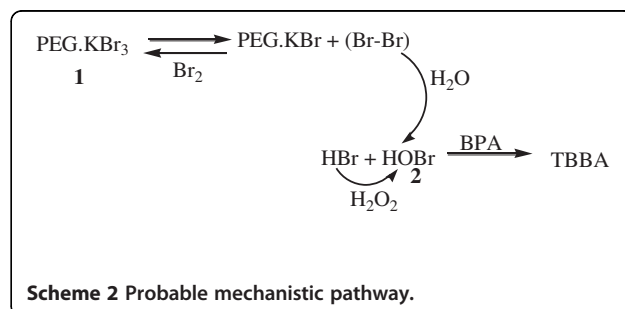
Experimental

General

All the substrates and reagents used were commercially available and were used without further purification. HPLC analyses were conducted using a Waters 2695 instrument (Meadow Instrumentation Inc, 10780, Bristol Rd, Bristol) with PDA detector, solvent system (70% CH₃CN + 30% H₂O), and a flow rate of 1 ml/min.

Preparation of [{K⁺PEG}-Br₃]**1**

In a round-bottomed flask (100 ml), bromine (68.6 mmol, 10.8 g, 3.5 ml) was added to a 34% aqueous solution of KBr (25 g; prepared by adding the 9 gm KBr in 135 g water) to prepare the solution of potassium tribromide. Polyethylene glycol (PEG₄₀₀; 27.4 g, 68.5 mmol) was added to the above solution, and the mixture was stirred for 5 h at room



Scheme 2 Probable mechanistic pathway.

temperature. The dark orange-red solution was extracted with dichloromethane, and the combined organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure. The dark orange-red viscous liquid **1** was obtained in quantitative yield (44.5 g, 97%). Infrared (IR) (cm^{-1}): 3,410 (OH), 1,112 ($\text{CH}_2\text{-O-CH}_2$), and 548 (Br-Br); analytical calculations of $[\text{K}^+\{\text{PEG-Br}_3\}]$ are as follows: calculated C, 31.85%; H, 5.60%; K, 5.75%; found C, 31.82%; H, 5.66%; K, 5.72%. The loading of the KBr_3 in the prepared reagent **1** was found to be 1.2 mmol/g.

General procedure for the synthesis of TBBPA

In to a 100-ml round-bottomed double-necked flask containing bisphenol A (0.23 g, 1 mmol) and water (5 ml), $[\text{K}^+\{\text{PEG-Br}_3\}]$ **1** (3.4 g, 5 mmol) was added with the mole ratio of 1:5, and the resulting mixture was stirred at room temperature until the color of the bromine disappeared. The progress of the reaction was monitored by TLC; after completion, the product was separated by filtration, and the residue so obtained was used for the regeneration of reagent **1** by the addition of molecular bromine in a controlled manner. The crude product was purified by crystallization with hot water. The yield of the TBBPA (98%) and purity of the product were found to be 99.2 (as analyzed by HPLC). The identity of the product was confirmed by its spectroscopic analysis. The characterization data of TBBPA are given as follows: M.Pt., 182°C ; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ , 7.25 (4H, s), 5.79 (2H, s), and 1.58 (6H, s). IR: (KBr) 3,514; 3,479; 2,986; 1,552; 1,470; 1,392; 1,321; 1,270; 1,160; 1,127; 865; 776; 731; 707; and 615 cm^{-1} . The analytical calculation is as follows: calculated C, 33.08%; H, 2.20%; found C, 32.78%; H, 2.24.

Conclusion

In summary, we have developed for the first time an efficient, simple, and easily recyclable brominating agent for the selective bromination of BPA to TBBPA in excellent yield and of high purity using $[\text{K}^+\{\text{PEG-Br}_3\}]$ as brominating agent. The developed reagent has many advantages such as the use of cheap and environmentally benign PEGs, facile regeneration, nonproduction of HBr as waste, efficient recycling, and higher yields of the desired product in mild reaction conditions.

Competing interests

Authors have filed a patent in India on the process described in the manuscript.

Authors' contributions

SV has done all the experiments mentioned in the manuscript, SLJ and BS provided the technical supported and drafted the manuscript. All authors have read and approved the manuscript.

Authors' information

SV have received an Indo-French Research fellowship under sandwich research programme. SLJ is currently holding a position of Senior Scientist at CSIR-Indian

Institute of Petroleum and has received many prestigious National Awards for her work in Synthetic Organic Chemistry.

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