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$\{[K.18\text{-Crown-6}]Br_3\}_n$: a unique tribromide-type and columnar nanotube-like structure for the oxidative coupling of thiols and bromination of some aromatic compounds

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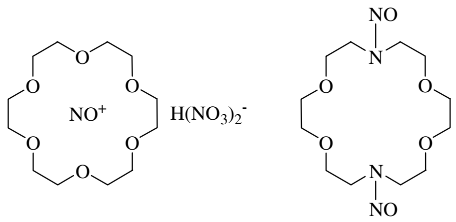
Abstract—Reaction of 18-crown-6 with KBr and then with bromine (Br_2) afforded a unique tribromide salt with a nanotube-like structure ($\{[K.18\text{-crown-6}]Br_3\}_n$). Oxidative coupling of thiols and bromination of some aromatic compounds is the first report on the chemistry of this reagent.

1. Introduction

Crown ethers have attracted significant attention from various field of science. Crown ether moieties are popular host compounds in host–guest chemistry and these ligands have shown a remarkable ability to form strong complexes with organic and inorganic cations[1] or anions,[2] selectively. Among the crown ethers, 18-crown-6 forms a very stable complex with K^+, which has the maximum stability constant compared with other alkali complexes involving metal cations.[3]

Organic tribromide reagents (OTBs) are preferable as oxidants to molecular bromine, owing to the hazards associated with elemental bromine. Several tribromides have been reported, that is, tetramethylammonium tribromide,[4] phenyltrimethylammonium tribromide,[5] cetyltrimethylammonium tribromide, tetrabutylammonium tribromide,[6] 1,8-diazabicyclo[5,4,0]-tetrabutylammonium tribromide,[7] pyridine hydrobromide perbromide,[8] hexamethylenetetramine-bromine,[9] and DABCO-bromine.[10] Recently some ionic liquid tribromides (IL-Br_3^-) for the preparation of bromoesters from aromatic aldehydes[11] and bromination of aromatic substrates[12] were reported. It would be extremely useful to



1 **2**

Figure 1.

Figure 2. Crystals of (**3**).

Keywords: $\{[K.18\text{-Crown-6}]^+Br_3^-\}_n$; 18-Crown-6; Tribromide; Nanotube-like; Bromination; Columnar; Oxidative coupling; Thiols; Host–guest chemistry.

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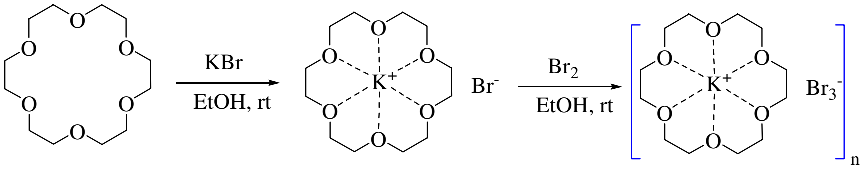


3

Scheme 1.

develop further synthetic protocols for the synthesis of OTBs.[13]

In continuation of our studies on the host–guest chemistry of crown ether **1**,[14] nitrosation of azacrown ethers **2**[15] (Fig. 1), oxidative coupling of thiols,[16] and bromination,[17] we found that when Br_2 was added to the complex [K.18-crown-6]Br, the unique tribromide reagent **3** was formed easily and after recrystallization from acetonitrile, nice red crystals were obtained (Fig. 2 and Scheme 1).

Crystallographic analysis confirmed the formulation of these crystals as $\{[K.18\text{-crown-6}]Br_3\}_n$, in which the $[K.18\text{-crown-6}]^+$ cations are aligned in columnar[18] stacks separated by bridging tribromide anions (Figs. 3 and 4). Each tribromide ligand spans two K^+ ions, although the coordination is far from linear, with Br–Br–K angles of 83.2°. Thus the columnar stacks are infinite one-dimensional polymeric chains of alternating cations and anions. The coordination geometry in the $[K.18\text{-crown-6}]^+$ cation is unremarkable.

We have found that this reagent can be used for the fast oxidative coupling of thiols, and bromination of aromatic compounds under mild conditions (Scheme 2 and Tables 1 and 2).

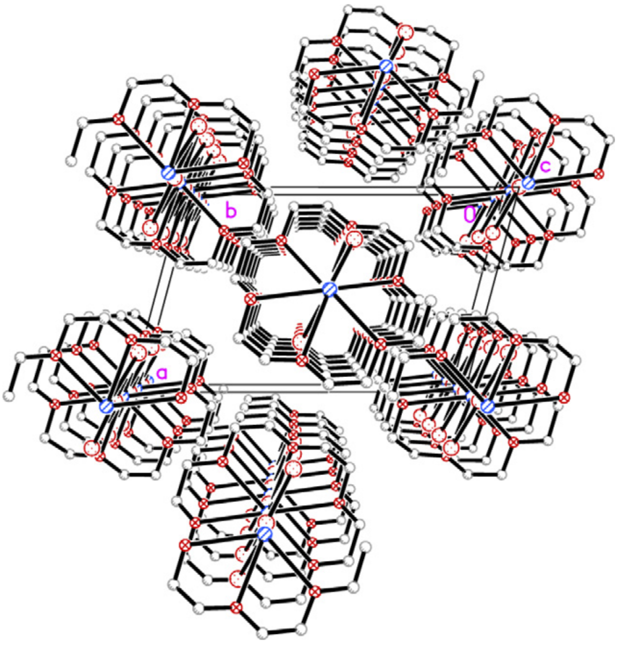


Figure 3. X-ray structure of $\{[K.18\text{-crown-6}]Br_3\}_n$.

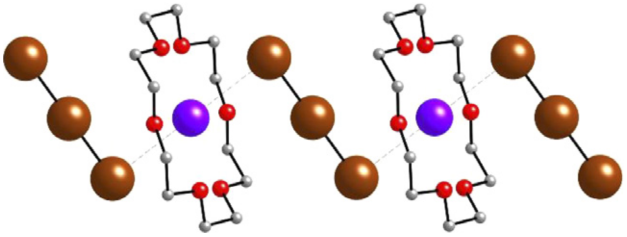
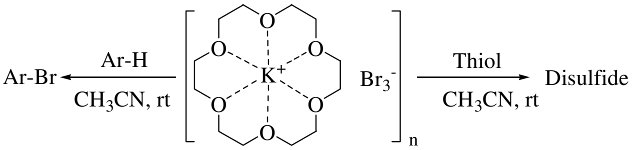
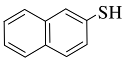
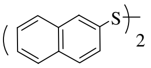
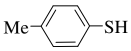
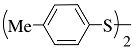
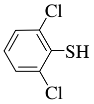
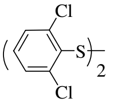
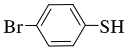
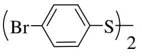
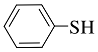
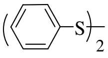
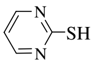
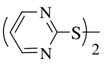
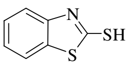
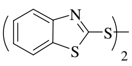


Figure 4. View of X-ray structure of $\{[K.18\text{-crown-6}]Br_3\}_n$ from another perspective.



Scheme 2.

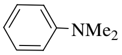
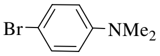
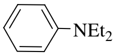
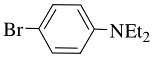
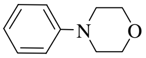
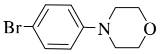
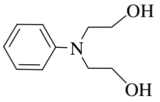
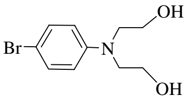
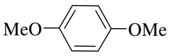
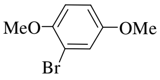
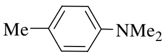
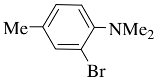
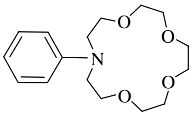
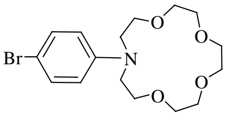
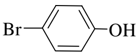
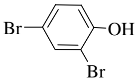
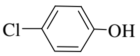
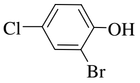
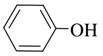
Table 1. Rapid coupling of thiols using $\{[K.18\text{-crown-6}]Br_3\}_n$ in acetonitrile at room temperature under mild conditions

Entry	Substrate	Product	Reagent/ substrate (mmol)	Yield (%)
1			1.1	86[a]
2			1.1	100[b]
3			1.1	100[b]
4			1.1	100[b]
5			1.1	100[b]
6			1.1	Sluggish
7			1.1	Sluggish

[a] Isolated yield.

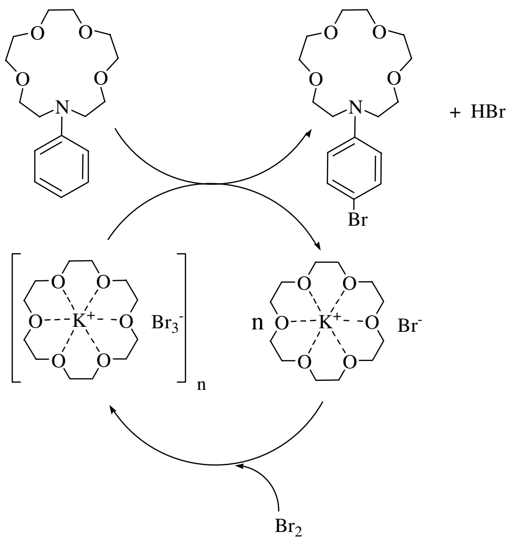
[b] Conversion.

Table 2. Rapid bromination of aromatic compounds using $\{[K.18\text{-crown-6}]Br_3\}_n$ in acetonitrile at room temperature under mild conditions

Entry	Substrate	Product	Reagent/substrate (mmol)	Yield[a] (%)
1			1	70
2			1	73
3			1	85
4			1	74
5			1	60
6			1	57
7			1	56
8			1	75
9			1	37
10		—	1	Sluggish

[a] Isolated yield.

To investigate the recyclability of the [K.18-crown-6]Br complex, the residue after work-up was washed with ethanol and Br_2 was added. The yellow solid obtained was recrystallized from acetonitrile. $\{[K.18\text{-Crown-6}]Br_3\}_n$ was generated again and brominated the aromatic amines successfully (Scheme 3). Also the oxidative coupling of thiols was reproduced by recycled $\{[K.18\text{-crown-6}]Br_3\}_n$ as efficiently as with a fresh sample.



Scheme 3.

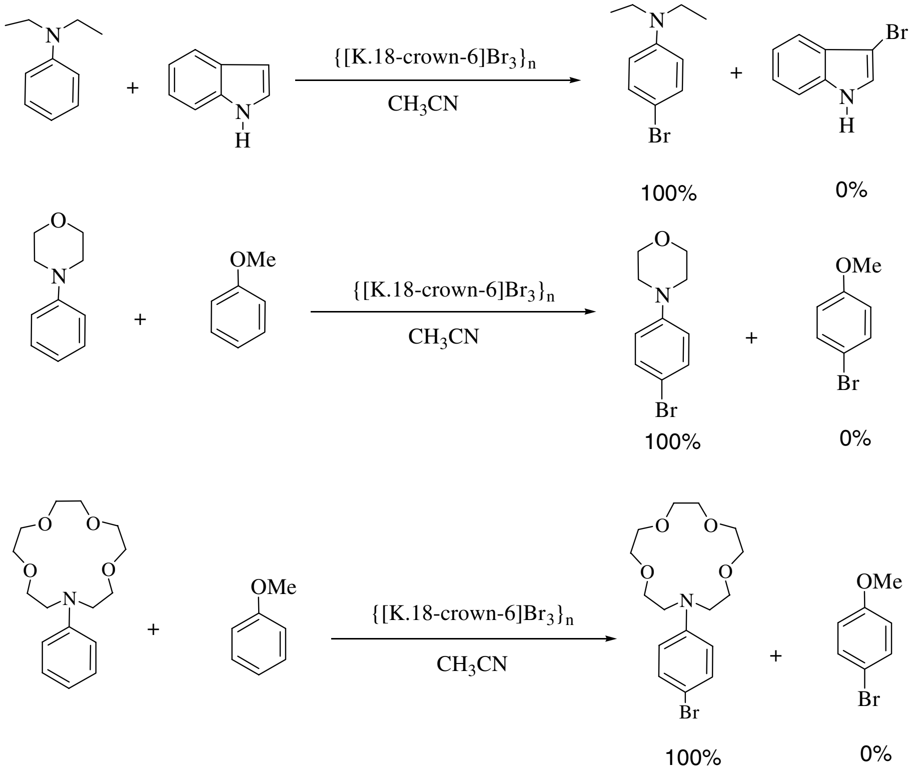
Competitive reactions were designed. Mixtures of equal amounts of aromatic substrates were subjected to bromination in the presence of $\{[K.18\text{-crown-6}]Br_3\}_n$ and good chemoselectivity was observed (Scheme 4).

In conclusion, the ability of $\{[K.18\text{-crown-6}]Br_3\}_n$ to generate bromine in the reaction media will be useful for organic functional group transformations.[19]

2. Experimental

2.1. Preparation of $\{[K.18\text{-crown-6}]Br_3\}_n$

In a round-bottomed flask (100 mL) equipped with a magnetic stirrer, KBr (0.95 g, 8 mmol) was added to a solution of 18-crown-6 (1.32 g, 5 mmol) in ethanol (30 mL) and the mixture stirred for 1 h, then filtered. Bromine (0.8 g, 5 mmol) was added to the solution.



Scheme 4.

After filtration over a sintered glass funnel, a fine yellow powder was obtained and recrystallized from CH_3CN to give red crystals [mp: 195–197 °C].

2.2. General procedure for reactions

$\{[K.18\text{-Crown-6}]Br_3\}_n$ was added to a solution of the substrate (1 mmol) in acetonitrile (4 mL) at room temperature (see Tables 1 and 2 for molar ratios). After immediate reaction, column chromatography on short pad of silica gel with CH_3CN afforded pure products in 37–86% yields.

2.3. Experimental description of the structure

An orange crystal ($0.35 \times 0.31 \times 0.30$ mm^3) was mounted on a Bruker SMART-1000 diffractometer. Crystal data: $C_{12}H_{24}Br_3KO_6$, $M = 543.14$, monoclinic, space group $P2_1/n$, $a = 8.955(5)$, $b = 8.054(5)$, $c = 14.082(8)$ Å, $\beta = 104.805(1)^\circ$, $V = 982.0(10)$ Å^3, $Z = 2$, $D_c = 1.837$, μ(Mo-Kα) $= 6.395$ mm^{-1}, $T = 150$ K. Refinement of 103 parameters with 2242 unique reflections afforded a final R_1 value [for selected data with $I > 2\sigma(I)$] of 4.04% and a final wR_2 value (all data) of 11.26%. Atoms K(1) and Br(2) lie on special positions such that only half of the complex cation and the tribromide anion lies in the asymmetric unit.

Acknowledgments

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