

**[M<sup>+</sup>.Crown.Y<sup>-</sup>] as a reagent**  
(M<sup>+</sup>= K<sup>+</sup>, NO<sup>+</sup>; Y<sup>-</sup>= Br<sub>3</sub><sup>-</sup>, I<sub>3</sub><sup>-</sup>, H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup>)

Compiled by Fateme Derakhshan-Panah

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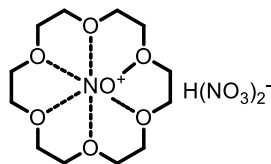


This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

### Introduction

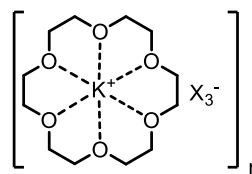
Crown ethers are heteroaromatic compounds that act as host compounds in Host-Guest chemistry [1], and can form complexes with organic or inorganic cations or anions [2]. Among the crown ethers, 18-Crown-6 has the potential to form stable complexes with cations such as K<sup>+</sup>, and NO<sup>+</sup>. These reagents have nanotube-like structures, their X-ray are presented in the following. Their preparation methods are given [3-5].

N<sub>2</sub>O<sub>4</sub> has been used in various forms in reactions. One of them is [NO<sup>+</sup>.Crown.H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup>] (Scheme 1), which has been used as recyclable and reusable reagent under homogeneous reaction condition [6].

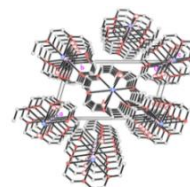


**Scheme 1.** Structure of [NO<sup>+</sup>.Crown.H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup>].

Moreover two other crown ether complexes, {[K.18-Crown-6]Br<sub>3</sub>}<sub>n</sub> and {[K.18-Crown-6]I<sub>3</sub>}<sub>n</sub>, have been shown as the trihalide reagents which are reusable and safety (Scheme 2) [3,4].



(a)



(b)



(c)

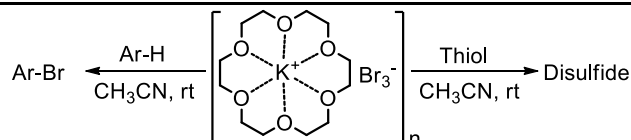


(d)

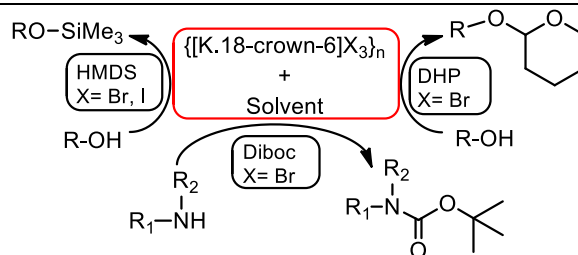
**Scheme 2.** (a) Structure of {[K.18-Crown-6]X<sub>3</sub>}<sub>n</sub>, X=Br, I; (b) X-ray structure of {[K.18-crown-6]Br<sub>3</sub>}<sub>n</sub>; (c) Crystal of {[K.18-crown-6]Br<sub>3</sub>}<sub>n</sub>; (d) Crystal of {[K.18-crown-6]I<sub>3</sub>}<sub>n</sub>.

## Abstracts

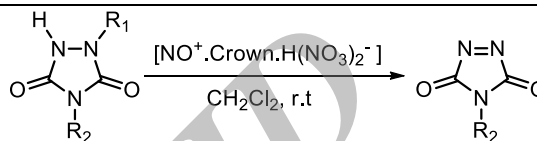
(A) {[K.18-Crown-6]Br<sub>3</sub>]<sub>n</sub> used for thiol coupling reaction and bromination of aromatic compounds in mild conditions [3].



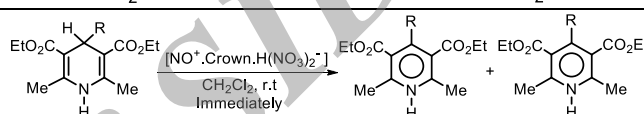
(B) {[K.18-Crown-6]X<sub>3</sub>]<sub>n</sub> has been also used for protection of alcohols and amines [4,7].



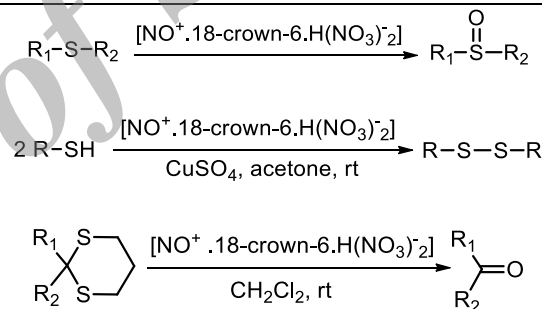
(C) Oxidation of urazoles to produce related triazolinediones was reported by using this reagent under mild conditions [8].



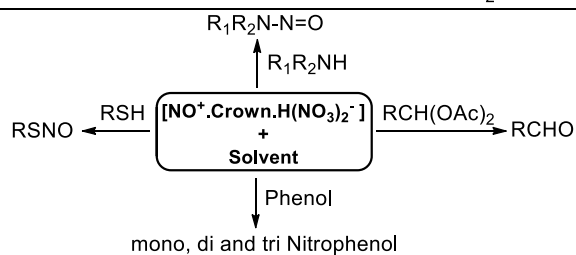
(D) Oxidation of dihydropyridines has been reported by the homogeneous system in presence of [NO<sup>+</sup>.Crown.H(NO<sub>3</sub>)<sub>2</sub>]<sup>-</sup>. Products are obtained at room temperature, short time and high Yield [9].



(E) [NO<sup>+</sup>.Crown.H(NO<sub>3</sub>)<sub>2</sub>]<sup>-</sup> has been used as nitrosation reagents for the preparation of thionitriles, also for obtain of disulfide from thiol and tionitrile, and has been used for deprotection of dithianes for preparation of sulfoxides [10].



(F) Various reactions has been reported by using the [NO<sup>+</sup>.Crown.H(NO<sub>3</sub>)<sub>2</sub>]<sup>-</sup> as a reagent, such as nitration of amine [11] and phenol [12], reproduction of aldehydes [13] and preparation of S-nitrosothiols from thiols [14].



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