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H₂O₂ as green and environmentally benign reagent for the oxidation of TMS ethers, THP ethers, and alcohols in the presence of {[K.18-Crown-6]Br₃}_n

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ABSTRACT

In the presence of {[K.18-Crown-6]Br₃}_n, a unique tribromide reagent, trimethylsilyl (TMS) ethers, tetrahydropyranyl (THP) ethers, and alcohols were oxidized to their corresponding aldehydes and ketones in H₂O₂. One-pot deprotection and oxidation of TMS ethers/THP ethers were performed directly and the conversion was complete. Avoiding the isolation of the corresponding alcohol as an intermediate step, the direct transformation of such substrates to carbonyls is the main aim of this work. {[K.18-Crown-6]Br₃}_n regeneration was performed via the addition of Br₂ to the residue of the reaction and recrystallization in acetonitrile.

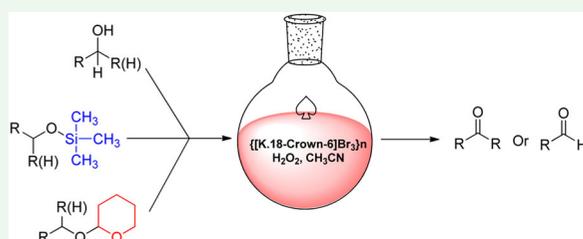
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Introduction

Owing to the importance of aldehydes and ketones as precursors and/or intermediates for numerous drugs, vitamins, and fragrances, the oxidation of alcohols to their corresponding carbonyl groups is of great importance compared to some other organic reactions (1). Most oxidation reactions require stoichiometric amounts of toxic reagent. Removal of the trace reagent from the reaction mixture is often costly and difficult. Therefore, in environment-friendly methods, oxidation reactions using cheap green oxidants, such as oxygen and hydrogen peroxide, have become increasingly popular (2).

Tetrahydropyranyl (THP) and trimethylsilyl (TMS) ethers are widely utilized in organic synthesis (3), and are the most versatile protective groups for alcohols due to their reasonable stability in nonacidic media. One of the attractive advantages of these protective groups is their ability to convert into carbonyl groups. Deprotective oxidation of THP and TMS ethers to their aldehydes or ketones is an important transformation in organic chemistry (4, 5).

Organic tribromides (OTBs) as reagents/catalysts are preferable to molecular bromine because of the high toxicity of elemental bromine. Some of these reagents include hexamethonium bis(tribromide) (6), poly(4-vinylpyridinium tribromide) (7), and tribromide ion immobilized on magnetic nanoparticle (8).

We reported {[K.18-crown-6]Br₃}_n as a particular tribromide type and columnar nanotube-like structure (I, Figure 1) in 2007. We have applied this compound to the bromination of aromatic rings, conversion of thiols to disulfides (9), and protection of amines and alcohols (10).

Previously, we have studied the oxidation of organic functional groups (11), especially oxidation of alcohols (12), using H₂O₂ derivatives, such as urea hydrogen peroxide (13), melamine-H₂O₂ (14), and polyvinylpyrrolidone-H₂O₂ (15), in various organic transformations. Consequently, the aim of this study was to evaluate the effect of {[K.18-crown-6]Br₃}_n as a unique tribromide reagent for oxidation of alcohols, TMS ethers, and THP ethers in the presence of H₂O₂.

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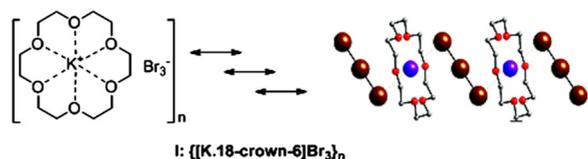


Figure 1. The structure of {[K.18-crown-6]Br₃}_n.

Experimental section

Chemicals were purchased from Merck. Products were characterized by comparison of their spectral (IR, ¹H-NMR, and ¹³C-NMR) with those of known samples. Preparation of {[K.18-crown-6]Br₃}_n and its recycling were performed according to our previously reported procedure (9).

General procedure for the oxidation of alcohols to aldehydes/ketones

To a solution of alcohols (1 mmol)/{[K.18-crown-6]Br₃}_n (2 mmol) in CH₃CN (8 mL) was added H₂O₂ 30% (1.1 mmol). The solution was stirred at reflux for the appropriate time (Table 1). The progress of the reaction was monitored by thin layer chromatography (TLC). After the completion of reaction, CH₃CN was removed by water-bath distillation. Column chromatography on short pad of silica gel with CH₃CN afforded pure products in good-to-excellent yields. {[K.18-Crown-6]Br₃}_n can regenerate (70%) via adding the Br₂ to the residue of the reaction and recrystallization in acetonitrile.

Table 1. Oxidation of alcohols, TMS ethers, and THP ethers to aldehydes/ketones using H₂O₂ in the presence of {[K.18-Crown-6]Br₃}_n.

Entry	Substrate (X=H, TMS, THP)	Time (min)			Isolated yields (%)		
		H ^a	TMS	THP	H	TMS	THP
1		30	37	42	85	89	92
2		28	36	42	87	92	78
3		30	32	35	81	82	90
4		41	45	47	82	87	84
5		23	29	32	91	83	86
6		33	37	37	95	90	87
7		22	29	32	81	92	78
8		27	36	39	82	84	89
9		25	35	35	93	85	65
10		26	35	39	88	87	89
11		21	40	45	94	78	63
12		31	38	44	88	93	79
13		37	44	52	90	79	70
14		32	36	45	93	76	79

^aUnder the reflux of CH₃CN.

General procedure for the deprotective oxidation of TMS ethers and THP ethers to aldehydes/ketones

H₂O₂ 30% (1.1 mmol) was added to the solution of TMS ethers or THP ethers (1 mmol)/{[K.18-crown-6]Br₃}_n (2 mmol) in CH₃CN (5 mL). The solution was stirred at reflux for the appropriate time (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, CH₃CN was removed by water-bath distillation. Column chromatography on short pad of silica gel with CH₃CN afforded pure products in good-to-excellent yields.

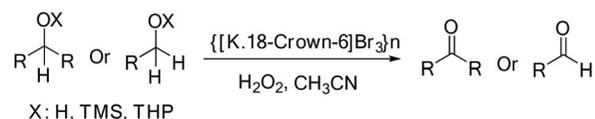
Results and discussion

In this study, we report that {[K.18-crown-6]Br₃}_n acts as an efficient reagent for the oxidation of alcohols, and direct conversion of TMS ethers and THP ethers to aldehydes/ketones. Control experiments were done to optimize the reaction conditions. First, oxidation of benzyl alcohol was used as a model reaction. This reaction was carried out in the presence of different amounts of {[K.18-crown-6]Br₃}_n, H₂O₂, and different solvents. The optimized reaction conditions were 2 mmol of {[K.18-crown-6]Br₃}_n, 1.1 mmol H₂O₂, and CH₃CN as the best solvent (Table 2).

Second, we converted a range of TMS ethers, THP ethers, and alcohols to their corresponding carbonyl groups under the optimized reaction conditions without any isolation of alcohols as intermediate (Scheme 1 and Table 1).

As seen in Table 1, a wide range of aliphatic and aromatic alcohols, TMS ethers and THP ethers could be converted to their corresponding aldehydes or ketones in high-to-excellent yields, and no over-oxidation products were observed under the reaction conditions.

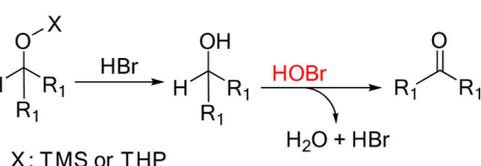
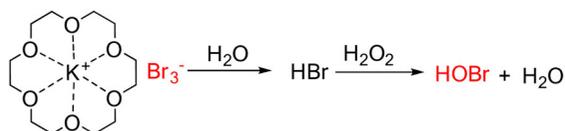
According to the previous reported paper (16) and our obtained results, we propose that the mechanism for the oxidation of alcohols, TMS ethers and THP ethers to aldehydes/ketones using H₂O₂ in the presence of {[K.18-Crown-6]Br₃}_n proceeds by the generation of HOBr that allows oxidation of alcohols and one-pot deprotective oxidation of TMS ethers and THP ethers (Scheme 2).



Scheme 1. Oxidation of alcohols, TMS ethers, and THP ethers to aldehydes/ketones.

Table 2. Optimization of the reaction condition for the oxidation of benzyl alcohol in the presence of $\{[K.18\text{-crown-6}]Br_3\}_n$, H_2O_2 and diversity of solvents.

Entry	$\{[K.18\text{-crown-6}]Br_3\}_n$ (mmol)	H_2O_2 (mmol)	Solvent (8 mL)	Temperature ($^{\circ}C$)	Time (min.)	Isolated yield (%)
1	2	–	–	25	30	Sluggish
2	2	–	CH_3CN	Reflux	50	Sluggish
3	1	1.1	CH_3CN	25	30	45
4	1.5	1.1	CH_3CN	Reflux	30	60
5	2	1	CH_3CN	Reflux	30	65
6	2	1.1	CH_3CN	Reflux	30	81
7	2	1.1	$CHCl_3$	Reflux	45	55
8	2	1.1	EtOAc	Reflux	45	67
9	2	1.1	THF	Reflux	45	71
10	2	1.1	<i>m</i> -hexane	Reflux	45	44



Scheme 2. Suggested mechanism for oxidation of alcohols and deprotective oxidation of TMS ethers and THP ethers to aldehydes/ketones using H_2O_2 in the presence of $\{[K.18\text{-Crown-6}]Br_3\}_n$.

Conclusions

In this research, we explain the oxidation of alcohols, and deprotective oxidation of TMS ethers and THP ethers to aldehydes/ketones using H_2O_2 in the presence of $\{[K.18\text{-Crown-6}]Br_3\}_n$. Avoiding the isolation of the corresponding alcohol as an intermediate step, the direct transformation of such substrates to carbonyls is the main aim of this work. $\{[K.18\text{-Crown-6}]Br_3\}_n$ can be regenerated via adding the Br_2 to the residue of the reaction and recrystallized it in acetonitrile. The reaction is carried out at reflux conditions and yields of products are good to excellent. We believe that this procedure will be a useful addition to existing methods for the oxidation of alcohols, TMS ethers, and THP ethers.

Disclosure statement

No potential conflict of interest was reported by the authors.

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