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Oxidative Cleavage of Benzyl Ethers by Use of Oxoaminium Salt

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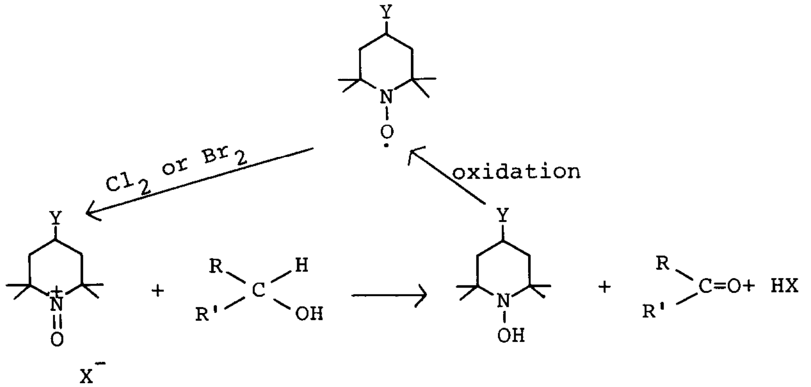
It was found that alkyl benzyl ether could be cloven by oxoaminium salt of 2,2,6,6-tetramethylpiperidine derivatives (1) to obtain benzaldehyde and the corresponding alkyl halide in excellent yield.

1-Oxo-2,2,6,6-tetramethylpiperidinium salt (I)[1] is known as an oxidizing agent of hydroxide ion,[2] and alcohols.[1,3,4] The recent reports of selective oxidation of alcohols[5,6,7] involve this oxoaminium ion as a mediator of redox system. Oxoaminium salt (1) is easily obtained by the halogen oxidation of the stable nitroxyl radical such as 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (2).



(1)

(I)

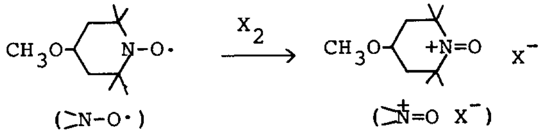
(II)

X=Br or Cl

R=alkyl
R'=H or alkyl

Some oxidative cleavage of benzyl ether by use of the stable cation radical of tris(p-bromophenyl)amines reported by W. Schmidt et al.[8]

We now report the new method for the oxidative cleavage of benzyl ether by use of oxoaminium salt. Actually, 4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium bromide (1a) and chloride (1b)[3] were used as oxidizing reagents.



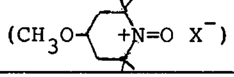
(2)

(1)

(1a):X=Br
(1b):X=Cl

As shown in Table 1, various benzyl ethers were oxidized with oxoaminium salts

Table 1. Oxidative cleavage of benzyl ether ($PhCH_2$-O-R) by use of oxoaminium salts.[a]



Ether R	Oxoaminium Salt		H_2O eq	Time	Products Y(%)		Recovered starting material(%)
	X	eq			PhCHO	RX	
CH_3	Br	1	-	17 hr	33	-	34
		2	-	17 hr	50	-	0
	Cl	1	-	20 min	2	-	95
		1.5	-	2 hr	7	-	82
		2	-	17 hr	11	-	67
C_5H_{11}	Br	1	-	17 hr	32	0	14
		2	-	17 hr	30	0	0
		1	3	2.5 hr	37	0	26
		2	3	5 hr	50	0	0
$PhCH_2$	Br	1	-	3 hr	38	16	46
		2	-	3 hr	49	38	14
		3	-	3 hr	63	35	0
		1	3	3 hr	47	0	53
		2	3	6 hr	70	0	30
		3	3	8 hr	100	0	0
	Cl	1	-	20 min	5	-	87
		1.5	-	2 hr	13	-	87
		2	-	17 hr	18	-	82

a) in methylene chloride at 30°c.

to obtain benzaldehyde. Benzyl methyl ether was oxidized with 2 eq. of (1a) at room temperature in methylene chloride to give benzaldehyde quantitatively. However, the yield of benzaldehyde was low in the case of using (1b), because oxoaminium chloride (1b) is less stable than (1a). Dibenzyl ether was also oxidized by oxoaminium bromide (1a) to give benzaldehyde and benzyl bromide. When 3 eq. of water was added in the reaction mixture of dibenzyl ether and (1a), 2 eq. of benzaldehyde was obtained. These results suggest that benzyl cation may form as an intermediate of the reaction.

Oxoaminium ion may be employed as electron transfer agent, as shown in eq.(a). Initially, lone pair electron of ether may transfer to oxoaminium salt to produce cation radical and subsequently deprotonation and bond cleavage will take place according to the following reaction scheme:

$$\mathrm{PhCH_2OCH_2Ph} + \underset{(1a)}{>\overset{+}{\mathrm{N}}\mathrm{=O\ Br^-}} \longrightarrow \underset{(3)}{\left[\mathrm{PhCH_2\overset{\cdot+}{O}CH_2Ph\ Br^-}\right]} + \underset{(2)}{>\mathrm{N{-}O\cdot}} \qquad \mathrm{(a)}$$

$$\underset{(3)}{\left[\mathrm{PhCH_2\overset{\cdot+}{O}CH_2Ph\ Br^-}\right]} \xrightarrow[\mathrm{-HBr}]{>\overset{+}{\mathrm{N}}\mathrm{=O\ Br^-}} \underset{(4)}{\left[\mathrm{PhCH\overset{+}{O}CH_2Ph}\right]} + >\mathrm{N{-}O\cdot} \qquad \mathrm{(b)}$$

$$\underset{(4)}{\left[\mathrm{PhCH\overset{+}{O}CH_2Ph}\right]} + \mathrm{Br^-} \longrightarrow \mathrm{PhCHO} + \mathrm{PhCH_2Br} \qquad \mathrm{(c)}$$

$$\underset{(4)}{\left[\mathrm{PhCH\overset{+}{O}CH_2Ph}\right]} + \mathrm{H_2O} \longrightarrow \mathrm{PhCHO} + \begin{array}{l}\mathrm{PhCH_2OH}\\ \big\downarrow\ >\overset{+}{\mathrm{N}}\mathrm{=O\ Br^-}\\ \mathrm{PhCHO} + >\mathrm{N{-}OH} + \mathrm{HBr}\end{array} \qquad \mathrm{(d)}$$

As shown in eq.(c), (4) is cloven to give benzaldehyde and benzyl cation, which reacts with bromide ion to obtain benzyl bromide subsequently, under none aqueous condition. The existence of water resulted in another products, as shown in eq.(d). Namely, (4) is cloven to obtain benzaldehyde and benzyl alcohol. Subsequently, benzyl alcohol is oxidizing with oxoaminium bromide (1a) to give benzaldehyde. The oxidation rate of benzyl alcohol to benzaldehyde is much faster than that of electron transfer shown in eq.(a).[3] From these reasons dibenzyl ether is cloven with oxoaminium salt under aqueous condition to give 2 eq. of benzaldehyde.

The benzyl ether function is one of the most common protecting groups for alcohols. Our method may use as the oxidative deprotection of benzyl ether. Deprotected alcohols are more oxidized with oxoaminium salt to produce the corresponding carbonyl compounds. From these results, oxoaminium salt is an excellent reagent of deprotection of benzyl ether of alcohol and oxidizing agent of alcohols to corresponding carbonyl compounds at the same time. Hydroxylamine ($>$N-OH), which is obtained after oxidation, can be reoxidized with chlorine or bromine to oxoaminium salt and reused as oxidizing agents.

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