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AEROBIC OXIDATION OF BENZYLIC HALIDES TO CARBONYL COMPOUNDS WITH MOLECULAR OXYGEN CATALYZED BY TEMPO/KNO₂ IN AQUEOUS MEDIA

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Benzylic halides were successfully oxidized to the corresponding aldehydes and ketones in good to excellent yields in aqueous media with molecular oxygen as oxidant in the presence of catalytic amounts of TEMPO (2,2,6,6-tetramethylpiperidyl-1-oxy) and potassium nitrite (KNO_2).

Keywords: Benzylic halide; oxidation; potassium nitrite; TEMPO

INTRODUCTION

The oxidation of benzylic halides to the corresponding aldehydes and ketones is an important fundamental reaction and of great significance in both laboratory and industrial synthetic chemistry. In many cases, direct oxidation of benzylic halides to aldehydes and ketones affords a more convenient synthesis than the oxidation of the corresponding alcohols. Of these, the best classical methods are the Sommelet^[1] and Hass-Bender^[2] reactions, but others such as the Kröhnke^[3] reaction and Kornblum^[4] oxidation are still commonly employed. Other procedures, such as oxidations with certain amine N-oxide,^[5-7] N-alkoxypyridinium salts,^[8] sodium periodate-dimethylformamide,^[9] selenium compounds,^[10] o-iodoxybenzoic acid (IBX),^[11] MnO₂ under neutral conditions,^[12] chromium-based reagents,^[13] and metal nitrates,^[14–17] have all been developed for this transformation. Because of the deterioration of the environment, the oxidation of benzylic halides with environmentally benign oxidants such as hydrogen peroxide^[18-21] and molecular oxygen^[22-24] has emerged quietly. In fact, Hashemi and Beni^[23] have reported a very simple and convenient procedure for oxidation of primary and secondary aryl/alkyl halides to carbonyl compounds, which uses molecular oxygen and CuCl/Kieselguhr as catalyst. Itoh and co-authors^[24] have also reported the photo-oxidation of aryl bromides

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Scheme 1. TEMPO/KNO₂-catalyzed oxidation of 4-isopropylbenzyl bromide by O_2 in aqueous media.

with mesoporous silica FSM-16 using dioxygen as the oxidant. Although these methods have the advantage that oxygen is used as the oxidant, volatile organic solvents such as acetone, hexane, or dichloromethane are also used. This defeats the aim of reducing the environmental burden of volatile organic contaminants. Therefore, the introduction of a new, economical, convenient, and ecofriendly method for oxidation of organic halides is still in demand.

In continuation of our ongoing program to develop organic-solvent- and transition-metal-free catalytic systems for chloromethylation^[25] and oxidation reactions,^[17] herein we report a highly efficient catalytic system consisting of KNO₂ and 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO) for the aerobic oxidation of benzylic halides to aldehydes and ketones with molecular oxygen in aqueous media. Our inspiration arises from the results of the NaNO₂/TEMPO systems for aerobic alcohol oxidation.^[26–29]

The oxidation of 4-isopropylbenzyl bromide (1a, 0.50 mol) was first carried out by vigorously stirring the two-phase system (1a and 15 mol H₂O) at reflux temperature in the presence of 5 mol% KNO₂ and 3 mol% TEMPO under an O₂ atmosphere (Scheme 1). The oxidation proceeded smoothly, and 72.5% isolated yield of 4-isopropylbenzaldehyde (2a) was obtained with 76.3% conversion after 3.5 h (Table 1, entry 1). Increasing the amount of H₂O to 30 mol, 99.0% conversion and 84.2% isolated yield were obtained at the same interval (entry 2). Under the present reaction conditions, overoxidation product (4-isopropylbenzoic acid) was not observed, and the main by-product was 4-isopropylbenzyl alcohol, which could be fully converted into 2a with yield of 92% by prolonging the reaction time to 4.0 h (entry 3). However,

Entry	KNO ₂ (mmol)	TEMPO (mmol)	H ₂ O (mol)	Time (h)	Con. (%) ^b	Yield (%) ^c
1	25.0	15.0	15.0	3.5	76.3	72.5
2	25.0	15.0	30.0	3.5	99.0	84.2
3	25.0	15.0	30.0	4.0	99.7	92.0
4	25.0		30.0	4.0	99.5	59.5 ^d
5		15.0	30.0	4.0	99.2	19.0 ^e

Table 1. Optimization of the reaction conditions for oxidizing 4-isopropylbenzyl bromide to 4-isopropylbenzaldehyde^a

^{*a*}Reaction conditions: 4-isopropylbenzyl bromide (0.5 mol), reflux, under O_2 atmosphere. ^{*b*}Conversions are based on the GC with area normalization.

^cIsolated yields.

^d30 g cumenic acid was obtained from the distillated residue.

^eThe main product (76%) was 4-isopropylbenzyl alcohol.

Table 2.	Catalytic	aerobic	benzvlic	halide	oxidation	in	aqueous	media ^a
1	caracycie		001123110		omaarron		aqueous	meand

	$R^1 \longrightarrow R^2$	TEMPO/KNO ₂ O ₂ , H ₂ O, reflux R ¹	Å R ²	
Entry	Organic halide	Product	Time (h)	Yield (%) ^b
1)—(() —Br	}-∢_у-сно	4	92
2	$\succ a$	}-∕С}-сно	5	89
3	d a	<u> </u>	5	91
4	Br	ССНО	3.5	95
5	C	ССНО	4	92
6	Br	Br	10	70^c
7	XCC	<u> СНО</u> СНО	4	90
8	–∕S→Br		5	85
9	X Br	СНО	6	81
10	Br	СССНО	3	87
11	e citation de la cita	ССНО	2	89
12	H ₃ CO ^{CI}	H3CO CHO	1.5	15 ^d
13	O ₂ N Br	O2N CHO	24	49 ^e

Entry	Organic halide	Product	Time (h)	Yield (%) ^t	
14	∬CI S	CHO	4	86 ^f	
15	G N Br	a N CHO	15	93	
16	H₃CO-⟨⟩⟨ ^{Br}	н₃со-{}_{	1	87	
17)-{C}Br	$\succ \sim$	3	94	
18	C Br	0 [°] O	1	90	
19	a⊣{_}_{	a-{{}}-{°	4	90	
20	O₂N-⟨Br	02N-{	12	89	
21	CT Br	CT-P	3.5	92	
22	C) ~~ CI	g	6	nd	
23	₿ ^r	h	24	_	

Table 2. Continued

^{*a*}Reaction conditions: halide (0.5 mol), KNO₂ (25 mmol), TEMPO (15 mmol), H₂O (30 mol), reflux, under O₂ atmosphere. In the case of chloride, 10 mol% KBr (50 mmol) was added.

^bIsolated yield.

^cPartial polymerization occurred with vacuum distillation.

 d 1-(Dimethoxymethyl)4-methoxybenzene (23%) and 4,4-oxy-bis-(methylene)diphenol (28%) were formed as two by-products.

^e45% of starting material was recovered.

^f5-Bromo-thiophene-2-aldehyde was formed as major by-product in 4.5%.

^gAn intractable mixture.

^hNo oxidation reaction was observed.

in the absence of TEMPO, further oxidation of **2a** to 4-isopropylbenzoic acid occurred (entry 4). The KNO₂ was also crucial for achieving good yields of **2a** because the yield decreased to 19% (entry 5) in the absence of KNO₂ but increased to 92% (entry 3) in the presence of KNO₂. Further experiments demonstrated the oxidation reaction could not be carried out under anhydrous conditions. At lower temperatures, such as 70 or 90 °C, this oxidation reaction proceeded very slowly. Therefore, the optimal reaction conditions were as follows: 0.5 mol of bromide,

3 mol% of TEMPO, 5 mol% of KNO₂, 30 mol of H₂O, at reflux and under an O₂ atmosphere.

Under these conditions, various benzyl halides were converted into their corresponding aldehydes (Table 2, entries 1-13). Benzyl chlorides were much less reactive than the corresponding bromides, but the reaction activity could be enhanced significantly by addition of a catalytic amount of 10 mol% KBr. The electron-neutral benzyl halides could be easily oxidized to the corresponding aldehydes and afford good to excellent isolated yields. However, electron-rich 4-methoxybenzyl chloride gave only 15% isolated yield of 4-methoxybenzaldehyde (entry 12) with two by-products: 1-(dimethoxymethyl)-4-methoxybenzene (23%) and 4,4-oxy-bis-(methylene)diphenol (28%). When substrates that possess a strongly electron-withdrawing nitro group were used, the yield was somewhat less than the yields for the other reactions, and 45% of the starting material was recovered after 24h (entry 13). The oxidation of 2-chloromethylthiophene gave the desired thiophene-2-carbaldehyde along with 5-bromo-thiophene-2-aldehyde as major by-product (entry 14). As for the oxidation of 5-(bromomethyl)-2-chloropyridine, a longer reaction time (15h) was needed to obtain full conversion and 93% isolated yield of 6-chloronicotinaldehyde (entry 15).

The corresponding ketones were obtained from the secondary benzylic halides (Table 2, entries 16–21). The reaction rate of the secondary halides was obviously faster than that of primary halides. Because of the presence of a double bond, cinnamyl chloride was oxidized to give an intractable mixture (Table 2, entry 22), and no efforts were made to isolate the resulting aldehydes from the mixture. The oxidation of 2-bormoethylbenzene, an aliphatic halide, could not be achieved in the catalytic process (Table 2, entry 23).

A possible overall mechanism for the oxidation of bromides, similar to that of alcohol, proposed by Liu and coworkers,^[26–29] is shown in Scheme 2. Hydrolysis of starting material 1 yielded the corresponding alcohol 2 and HBr. The oxidation of the resulting alcohol into carbonyl compounds was realized by oxoammonium cation, an active oxidant of alcohols,^[30–32] which could be continuously obtained in cycle I by oxidizing TEMPOH, the reduced form of TEMPO, with Br₂, and the latter was reduced into HBr, which initially came from the hydrolysis of bromides. The reoxidation of HBr to Br₂ by NO₂ is shown in cycle II. NO₂ was reduced to NO



Scheme 2. Proposed overall mechanism.

when it completed the oxidation of HBr. The oxidation of NO into NO_2 could be easily performed with molecular oxygen (cycle III). The hydrolysis of halides was a reversible process, and increasing the amount of water used could lead to a faster reaction rate. In the oxidation of benzylic chlorides, addition of catalytic amount of KBr was helpful to this reaction by producing the HBr, which played an essential role in the catalytic cycle. It looks likely that the hydrolysis of the halides was the rate-controlling step. Secondary halides hydrolyzed faster than primary ones, so that they were oxidized faster.

CONCLUSION

In summary, we have found a useful method for aerobic oxidation of benzylic halides directly to the corresponding aldehydes and ketones in aqueous media under an O_2 atmosphere with catalytic amounts of TEMPO and KNO₂. Water was used as both reagent and solvent, and no organic solvents were used in the whole process. Although the reaction does not work for aliphatic halides, lack of transition metals, simple reaction conditions, and good to excellent yields make this method an attractive synthetic tool for the oxidation of benzylic halides to corresponding aldehydes or ketones.

TYPICAL EXPERIMENTAL PROCEDURES

The typical experimental procedure is exemplified by the oxidation of 4isopropylbenzyl bromide in a 1000-mL, round-bottomed flask equipped with a mechanic stirrer, a thermometer, and a reflux condenser. The bromide (0.5 mol), TEMPO (15 mmol), and KNO₂ (25 mmol) were stirred vigorously at reflux in H_2O (30 mol) under an O₂ atmosphere for 4 h. The reaction progress was monitored using an Agilent6890 gas chromatograph equipped with an HP-5MS capillary column $(30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ mm} \text{ ID})$ and a hydrogen flame detector. The gas chromatography (GC) conditions were as follows: injection port temperature was set at 280 °C and detector temperature at 300 °C. Inlet pressures of nitrogen gas and hydrogen gas were 65 KPa and 80 Kpa, respectively, and the amount of the test specimen was $0.1\,\mu L$. The temperature program started at 80 °C and maintained this temperature for 2 min, then ramped to 165 °C at 7 °C/min, again up to 250 °C at 25 °C/min, followed by 15 min at 250 °C. After completion, the organic layer was separated, washed with 20 wt% aqueous Na₂S₂O₃ solution and saturated aqueous NaHCO₃ solution to remove any trace of oxidant and TEMPO, dried over anhydrous Na₂SO₄, and finally distilled under vacuum to give pure 4-isopropylbenzaldehyde (bp: 86-87°C/5mmHg) in 92% yield identified by ¹H NMR and comparison to its authentic sample.

ANALYTICAL DATA OF NEW PRODUCTS

4,4-Oxy-bis-(methylene)diphenol (12)

Mp 33.5–35 °C, bp: 124–126 °C/5 mmHg. ¹H NMR (CDCl₃, 500 MHz): δ 4.46 (4H, s, –CH₂–), 6.89 (4H, d, *J*=14.5, ArH), 7.28 (4H, d, *J*=14.5, ArH), 9.52 (2H,

s, –OH). MS (m/z): 230 (M⁺), 229 (M⁺ – 1), 198 (M⁺ – 32), 153 (M⁺ – 77), 91 (M⁺ – 139), 77 (M⁺ – 153). Elemental analysis: C, 73.03%; H, 6.13%; calculated from $C_{14}H_{14}O_3$. Found: C, 72.90%; H, 6.12%.

6-Chloronicotinaldehyde (15)

Mp: 69.5–71.0 °C, bp: 117–119 °C/5 mmHg. ¹H NMR (CDCl₃, 500 MHz): δ 7.52 (H, d, J = 8.2, 5-PyH), 8.15 (H, q, J = 10.4, 4-PyH), 8.87 (H, d, 2-PyH), 10.14 (H, s, –CHO). MS (m/z): 142 (M⁺ + 1), 141 (M⁺), 113 (M⁺ – 28), 107 (M⁺ – 34), 79 (M⁺ – 62), 52 (M⁺ – 89). Elemental analysis: C, 50.91%; H, 2.85%; Cl, 25.05% calculated from C₆H₄CINO. Found: C, 50.79%; H, 2.85%; Cl, 24.99%.

3-Methyl-2-acetylbenzofuran (2I)

Mp: 23.5–24.5 °C, bp: 102–104 °C/5 mmHg. ¹H NMR (CDCl₃, 500 MHz): δ 2.57 (3H, s, –CH₃), 2.59 (3H, s, –CH₃), 7.28 (H, m, *J*=14.6, ArH), 7.46 (H, m, *J*=15.3, ArH), 7.48 (H, d, *J*=8.0, ArH), 7.60 (H, d, *J*=7.9, ArH). MS (m/z): 174 (M⁺), 173 (M⁺-1), 159 (M⁺-15), 131 (M⁺-43), 103 (M⁺-71), 77 (M⁺-97). Elemental analysis: C, 75.84%; H, 5.79% calculated from C₁₁H₁₀O₂. Found: C, 75.64%; H, 5.78%.

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