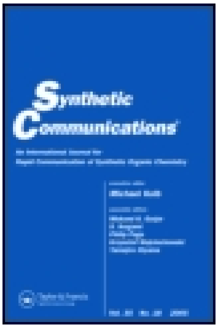

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Oxidation of Benzyl Halides to Aldehydes and Ketones with Potassium Nitrate Catalyzed by Phase-Transfer Catalyst in Aqueous Media

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Abstract: The catalytic oxidation of benzyl halides to aldehydes and ketones in aqueous media was studied under relatively mild reaction conditions by using phase-transfer catalyst combined with potassium nitrate and 10% aqueous potassium hydroxide solution. As a result, a simple high-yield procedure has been developed.

Keywords: Benzyl halide, oxidation, phase-transfer catalyst, potassium nitrate

INTRODUCTION

The oxidation of benzyl halides to the corresponding aldehydes and ketones is widely recognized as one of the most fundamental transformations in both laboratory and industrial synthetic chemistry because the aldehydes and ketones serve as important intermediates for the synthesis of perfumery chemicals, pharmaceuticals, dyestuffs, agrochemicals, and polymers.[1] Direct procedures for oxidizing benzyl halides to aldehydes and ketones, in many cases, afford more convenient synthesis than the oxidation of the corresponding alcohols.[2] Of these, two classic methods,

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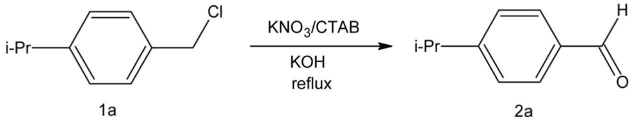
the Sommelet[3] and Hass–Bender[4] reactions, are the most straightforward and commonly employed, and while each has some limitations, one or other can almost always be satisfied for any given benzyl halide.[5] Other procedures, such as the Kröhnke[6] and Kornblum[7] methods and oxidations with different amine N-oxide,[8,9] N-alkoxypyridinium salts,[10,11] $NaIO_4$–DMF,[12] selenium compounds,[13] V_2O_5-H_2O_2,[14] IBX,[15] the Masaki photooxidation,[16] and mercury[5] and bismuth[17] nitrate salts, have all been developed with different degrees of success. Because of deterioration of the environment, the introduction of environmentally benign methods for oxidation of benzyl halides is still in demand.

Phase-transfer catalysis (PTC) is a versatile synthetic technique that has been widely applied to intensify otherwise slow heterogeneous reactions involving an organic substrate and an ionic reactant, either dissolved in water (liquid–liquid) or present in solid state (liquid–solid).[18] In addition, PTC can make reaction conditions gentle, can effectively avoid side reactions, can reduce consumption of organic solvent and raw materials, and can enhance the efficiency of organic synthesis. At present, PTC has been applied in various organic syntheses, such as electrophilic substitution reaction, nucleophilic substitution reaction, oxidation reaction, and hydrolysis.[19–21] We report here a new, economic, and convenient method by which benzyl halides can be directly oxidized to aldehydes and ketones with potassium nitrate (KNO_3) catalyzed by PTC without any organic solvents.

The oxidation of 4-isopropylbenzyl chloride (0.10 mol) was first carried out by vigorously stirring the two-phase system (4-isopropylbenzyl chloride and 15 mL H_2O) at reflux temperature with KNO_3 (0.11 mol). The yield of 4-isopropylbenzaldehyde, **2a**, was only 12% (Table 1, entry 1) after 10 h. Using cetyltrimethylammonium bromide (CTAB, 1.1 mmol) as PTC under the same conditions, **2a** was obtained in a higher yield 57% (Table 1, entry 2). The colors of the reaction mixture varied from colorless to yellow and a red-brown gas was observed as the reaction proceeded. After addition of 0.11 mol of potassium hydroxide (KOH) to the catalytic system, the yield of **2a** increased to 71% (Table 1, entry 3) within 4 h. These results show that KOH can promote this oxidation reaction to some extent. Considering that **2a** may decompose under the strongly basic conditions, we added 10% aqueous KOH solution (60 mL, 0.11 mol) dropwise with a dropping funnel to keep the pH value at 10–11 over the indicated time. The yields of **2a** were significantly increased. The results are shown in Table 1.

PTC and KOH must coexist in this oxidation system (Table 1, entries 4–6). The yield of **2a** was raised to 92% in a shorter period (4 h) if both CTAB and KOH were present in the reaction system (Table 1, entry 5). CTAB was also crucial for achieving high yields of **2a** because the yield

Table 1. CTAB-catalyzed oxidation of 4-isopropylbenzyl chloride with KNO_3 in aqueous media[a]



Entry	KNO_3 (mol)	CTAB (mmol)	KOH (mol)	Time (h)	Yield (%)[b]
1	0.11			10	12
2	0.11	1.1		10	57
3	0.11	1.1	0.11	4	71[c]
4	0.11[d]		0.11	4	39
5	0.11[d]	1.1	0.11	4	92
6	0.11[d]	1.2	0.11	4	91

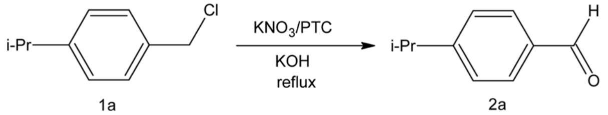
[a] Reaction conditions: 4-isopropylbenzyl chloride (0.1 mol), H_2O (15 mL), reflux.

[b] Isolated yield.

[c] About 2 g cumenic acid (mp: 117–119 °C, lit.[22] mp 118–120 °C) was obtained by acidifying the reaction aqueous solution with hydrochloric acid.

[d] Added 10% KOH aqueous solution (60 mL, 0.1 mol) dropwise over the indicated time with a dropping funnel.

Table 2. PTC-catalyzed oxidation of 4-isopropylbenzyl chloride with KNO_3 in aqueous media[a]



Phase-transfer catalyst	Time (h)	Yield (%)[b]
CTAB	4	92
TEAB	12	53
TBAB	8	71
DTAB	6	80

[a] Reaction conditions: 4-isopropylbenzyl chloride (0.1 mol), KNO_3 (0.11 mol), H_2O (15 mL), PTC (1.1 mmol); 10% KOH aqueous solution (60 mL, 0.11 mol) added dropwise with a dropping funnel over 4 h, reflux.

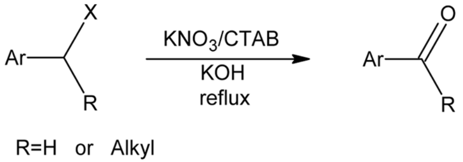
[b] Isolated yield.

decreased to 39% in the absence of CTAB (Table 1, entry 4) but increased to 92% in the presence of CTAB (1.1 mmol). Using 1.2 mmol of CTAB, under the same conditions, the yield was not enhanced significantly. At lower temperatures such as 70 or 90°C, this oxidation reaction proceeded very slowly. Therefore, the optimal reaction conditions were observed in Table 1, entry 5. Besides CTAB, we also tried to use tetraethylammonium bromide (TEAB), tetrabutylammonium bromide (TBAB), and dodecyltrimethylammonium bromide (DTAB) as PTCs in this catalytic oxidation system. However, the yields were merely 53%, 71%, and 80%, respectively (Table 2). The best PTC is CTAB.

Various benzyl halides could also be converted to the corresponding aldehydes/ketones under the same reaction conditions (Table 3). The benzyl halides with electron-withdrawing groups could be more easily oxidized to the corresponding aldehydes/ketones than those containing electron-releasing ones. Thus, many aldehydes/ketones with electron-releasing groups need longer reaction times to obtain higher yields (Table 3). The substrates with a strong electron-withdrawing nitro groups resulted in an intractable mixture (Table 3, entry 15), and all efforts to isolate the resulting aldehydes from the mixture failed. Further, the present catalytic oxidation system was not a good choice for the oxidation of 4-methoxybenzyl halides and gave only 25% isolated yield of 4-methoxybenzaldehyde with two by-products: 4-methoxybenzyl alcohol (34%) and 4-methoxybenzoic acid (35%). No aliphatic aldehydes could be produced through the oxidation of aliphatic halides under the same reaction conditions. The yield for oxidation of benzyl bromide to aldehydes/ketones was slightly higher than that for benzyl chloride (Table 3).

The oxidation mechanism in the present reaction system is well documented in the literature.[5] Because the formation of benzyl nitrate esters was observed in the reaction, we believe that benzyl halides were first transported to the corresponding nitrate esters by treatment with aqueous potassium nitrate solutions catalyzed by PTC and then transformation of the resulting nitrate ester into the corresponding aldehydes and ketones under the synergism of PTC and KOH. To confirm this speculation, we performed the reaction of 4-isopropylbenzyl chloride **1a** (0.1 mol) with potassium nitrate (0.11 mol) and 1.1 mmol of CTAB under our catalytic system at reflux for 1.5 h and found that 16.0 g (82%) of 4-isopropylbenzyl nitrate ester **3a** was indeed formed (Scheme 1). Elimination of nitrite acid from the resulting ester by KOH with the help of CTAB gave the desire 4-isopropylbenzaldehyde. Based on these results, we propose the plausible mechanism of the oxidation process shown in Scheme 1.

Table 3. CTAB-catalyzed oxidation of benzyl halides with KNO_3 in aqueous media[a]



Entry	Benzyl halide	Product	Time (h)	Yield (%)[b]	Bp (°C)	Lit. bp (°C)
1	$C_6H_5CH_2Cl$	C_6H_5CHO	3.0	90	40–42/5 mm	178.9[24]
2	$C_6H_5CH_2Br$	C_6H_5CHO	3.0	91	40–42/5 mm	178.9[24]
3	$4\text{-}CH_3C_6H_4CH_2Cl$	$4\text{-}CH_3C_6H_4CHO$	3.5	86	58–61/5 mm	205[24]
4	$4\text{-}CH_3C_6H_4CH_2Br$	$4\text{-}CH_3C_6H_4CHO$	3.5	89	58–61/5 mm	205[24]
5	$2\text{-}{}^iPrC_6H_4CH_2Cl$	$2\text{-}{}^iPrC_6H_4CHO$	4.0	92	84–85/5 mm	—
6	$4\text{-}{}^tBuC_6H_4CH_2Cl$	$4\text{-}{}^tBu\text{-}C_6H_4CHO$	4.0	90	97–99/5 mm	97–98/5 mm[25]
7	$3,4\text{-}(CH_3)_2C_6H_3CH_2Cl$	$3,4\text{-}(CH_3)_2C_6H_3CHO$	6.0	81	67–68.5/5 mm	96/12 mm[23]
8	$2,4,6\text{-}(CH_3)_3C_6H_2CH_2Cl$	$2,4,6\text{-}(CH_3)_3C_6H_2CHO$	7.5	82	61–63/5 mm	71/9 mm[26]
9	$4\text{-}{}^tBu\text{-}2,6\text{-}(CH_3)_2C_6H_2CH_2Cl$	$4\text{-}{}^tBu\text{-}2,6\text{-}(CH_3)_2C_6H_2CHO$	8.0	71	mp 128–129	—
10	$2\text{-}ClC_6H_4CH_2Cl$	$2\text{-}ClC_6H_4CHO$	3.0	87	61–63/5 mm	215[24]
11	$4\text{-}ClC_6H_4CH_2Cl$	$4\text{-}ClC_6H_4CHO$	3.0	89	mp 46–47	mp 47[24]
12	$4\text{-}BrC_6H_4CH_2Cl$	$4\text{-}BrC_6H_4CHO$	4.0	85	mp 66–68	mp 67[24]
13	$3\text{-}CH_3OC_6H_4CH_2Cl$	$3\text{-}CH_3OC_6H_4CHO$	6.0	77	85–87.5/5 mm	143/50 mm[24]
		$4\text{-}CH_3OC_6H_4CHO$		25	112–115/5 mm	245–248[27]
14	$4\text{-}CH_3OC_6H_4CH_2Cl$	$4\text{-}CH_3OC_6H_4CH_2OH$	0.25	34	118–120/5 mm	54/0.2 mm[23]
		$4\text{-}CH_3OC_6H_4COOH$		35	mp 186–187	mp 184–185[22]

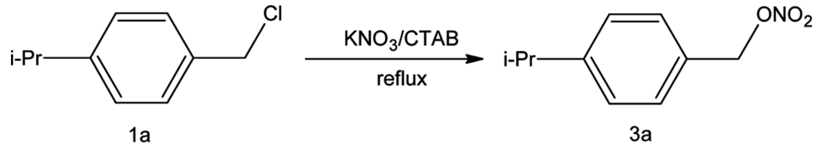
15	4-$NO_2C_6H_4CH_2Cl$	4-$NO_2C_6H_4CHO$	2.0	0^c	—	—
16	1-$C_{10}H_7CH_2Cl$	1-$C_{10}H_7CHO$	3.0	87	129–131/5 mm	161/15 mm[24]
17	4-$CH_3OC_6H_4CHClCH_3$	4-$CH_3OC_6H_4CHOCH_3$	1.2	63	mp 38–39	mp 36–38[24]
18	4-$FPhCHBrCH_3$	4-$FPhCOCH_3$	4.5	79	56–58/5 mm	196[24]
19	PhCHBrPh	PhCOPh	8.0	55	mp 48–49	mp 48.1[24]
20	$PhCH_2CH_2Br^d$	$PhCH_2CHO$	10.0	0		

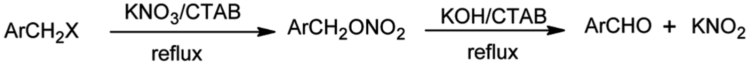
[a] Reaction conditions: benzyl halide (0.1 mol), KNO_3 (0.11 mol), H_2O (15 mL), CTAB (1.1 mmol), 10% KOH aqueous solution (60 mL, 0.11 mol) added dropwise with a dropping funnel over the indicated time, reflux.

[b] Isolated yield.

[c] An intractable mixture.

[d] 2-Bromoethylbenzene was used.





Scheme 1. Proposed mechanism for the oxidation of benzyl halides with KNO_3 catalyzed by CTAB and KOH.

CONCLUSION

In conclusion, we have developed a new, economic, convenient, and ecofriendly method for the preparation of aromatic aldehydes and ketones from benzyl halides. Judging from the conditions employed, this oxidation method showed has great prospects in industrial applications. Efforts to elucidate the scope and limitations of this oxidation system are under way.

EXPERIMENTAL

Typical Reaction Procedures

To the reaction mixture of 4-isopropylbenzyl chloride (16.8 g, 0.1 mol), KNO_3 (11.1 g, 0.11 mol), CTAB (0.4 g, 1.1 mmol), and H_2O (15 mL), 10% aqueous KOH solution (60 mL, 0.11 mol) was added dropwise with a dropping funnel to keep the pH value at 10–11 over 4 h at reflux with vigorous stirring. The reaction progress was monitored by GC Agilent 6890 with a FID and a DB-1701 column, 30 m × 0.25 mm i.d. At the end of the experiment, the organic product was extracted with ether (3 × 50 mL); washed with water to remove any traces of CTAB, KNO_3, and KOH; and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was distilled under vacuum to give pure 4-isopropylbenzaldehyde (bp: 86–87 °C/5 mmHg, lit.[23] 41–42 °C/1.20 mmHg) in 92% yield identified by ^1H NMR or its authentic sample.

Preparation of 4-Isopropylbenzyl Nitrate (3a)

A mixture of 4-isopropylbenzyl chloride (16.8 g, 0.1 mol), KNO_3 (11.1 g, 0.11 mol), CTAB (0.4 g, 1.1 mmol), and H_2O (15 mL) was heated to reflux for 1.5 h. After the reaction mixture was cooled to room temperature, it was extracted with ether (3 50 mL), washed with water to remove any traces of CTAB and KNO_3, and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was distilled under vacuum to give pure 4-isopropylbenzyl nitrate (**3a**, a colorless liquid, 16.0 g, 82%). Bp: 62–63 °C/5 mmHg. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.24 (6H, d, *J* = 6.9 Hz, CH_3), 2.87–2.97 (1H, m, CH), 5.39 (2H, s, CH_2), 7.26 (2H, d, *J* = 8.1 Hz, Ar), 7.32 (2H, d, *J* = 7.9 Hz, Ar). MS (m/z, %): 195 (M^+, 68), 196 ($M^+ +1$, 8), 180 ($M^+ -15$, 9), 149 ($M^+ -46$, 98), 133 ($M^+ -62$, 86), 119 ($M^+ -76$, 97), 105 ($M^+ -90$, 72), 91 ($M^+ -104$, 100), 79 ($M^+ -116$, 41). Elemental analysis: C, 61.53%; H, 6.71%, N, 7.18%; O, 24.58% calculated from $C_{10}H_{13}NO_3$. Found: C, 61.55%; H, 6.71%; N, 7.16%; O, 24.52%.

Analytical Data of New Products

2-Isopropylbenzaldehyde (5)

Bp: 84–85 °C/5 mm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.28 (6H, d, *J* = 7.8 Hz, CH_3), 2.98 (1H, m, CH), 7.44 (1H, dd, *J* = 8.2, 8.2 Hz, Ar), 7.49 (1H, d, *J* = 8.2 Hz, Ar), 7.82 (1H, d, *J* = 8.2 Hz, Ar), 8.05 (1H, s, Ar), 10.54 (1H, s, CHO). MS (m/z, %): 148 (M^+, 67), 147 ($M^+ -1$, 11), 133 ($M^+ -15$, 100), 119 ($M^+ -29$, 30), 105 ($M^+ -43$, 68), 77 ($M^+ -71$, 29). Elemental analysis: C, 81.04%; H, 8.16%; O, 10.80% calculated from $C_{10}H_{13}NO_3$. Found: C, 80.94%; H, 8.15%; O, 10.83%.

4-*tert*-Butyl-2, 6-Dimethylbenzaldehyde (9)

Mp: 128–129 °C, bp: 168–170 °C/5 mmHg. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.32 [9H, s, 4-$C(CH_3)_3$], 2.39 (6H, s, 2, 6-CH_3), 7.12 (2H, s, 3,5-Ar-H), 10.59 (H, s, CHO). MS (m/z, %): 190 (M^+, 45), 189 ($M^+ -1$, 58), 161 ($M^+ -29$, 12%), 147 ($M^+ -43$, 6.2), 133 ($M^+ -57$, 100), 119 ($M^+ -71$, 10), 91 ($M^+ -101$, 17), 77 ($M^+ -113$, 64). Elemental analysis: C, 82.06%; H, 9.53%; O, 8.41% calculated from $C_{10}H_{13}NO_3$. Found: C, 81.98%; H, 9.52%; O, 8.56%.

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