Oxidation of Benzyl Chlorides and Bromides to Benzoic Acids with 30% Hydrogen Peroxide in the Presence of Na₂WO₄, Na₂VO₄, or Na₂MoO₄ under Organic Solvent-Free Conditions

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Due to deterioration of the environment, "green chemistry" has been receiving increasingly more attention since the 1990s. In research of environment-benign oxidants, many chemists try to use hydrogen peroxide to substitute for the commonly used inorganic oxidants¹ because water is the sole expected side product.² Transition-metal-catalyzed oxidations with dilute hydrogen peroxide under phase-transfer conditions are particularly attractive because they are free of most drawbacks encountered in homogeneous systems and allow use of dilute aqueous solutions of the oxidant.^{3,4,5b} A number of chemists reported on the oxidation of primary and secondary alcohols to ketones and acids with hydrogen peroxide under aqueous/organic biphasic conditions, respectively.⁵ Later, it was found that some aliphatic and aromatic aldehydes could also be oxidized to acids under the same conditions.^{5f,6} However, it is well-known that benzaldehydes or benzyl alcohols are basically prepared from benzyl chlorides in industry or laboratory.⁷ Thus, direct oxidation of benzyl chlorides to benzoic acids by

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environmental benign method will be a more attractive and practical way from the point of view of synthetic chemistry. In fact, Yadav has found that capsule membrane supported phase-transfer-catalyzed (CM-PTC) oxidation of benzyl chloride using hydrogen peroxide as the oxidizing reagent. In that case, benzaldehyde was the major product.⁸ Recently, Kumar also reported that benzaldehyde could be successfully obtained using Ti silicates having Bronsted acidity in the presence of hydrogen peroxide and water through the oxidation of benzyl chloride.⁹

Herein, we wish to report that benzyl chloride 1a can be directly oxidized to the corresponding benzoic acid 2a in an eco-safer way using 30% hydrogen peroxide with $Na_2WO_4 \cdot 2H_2O$ as a catalyst and $[CH_3(n-C_8H_{17})_3N]^+HSO_4^$ as a phase-transfer agent (PTC) without any organic solvents (Scheme 1). The oxidation of benzyl chloride (10.0 mmol) was first carried out by vigorously stirring the biphasic reaction system (benzyl chloride and water) at 90 °C with a large excess of 30% H_2O_2 (4.1 mL, 36 mmol), Na₂WO₄·2H₂O (66 mg, 0.2 mmol), and [CH₃(n- $C_8H_{17})_3N]^+$ HSO₄⁻ (93 mg, 0.2 mmol). The yield of **2a** was only 15% (Table 1, entry 2). Using 30% H₂O₂ (3.0 mL, 26 mmol) under the same reaction conditions, 2a was obtained in a lower yield (8%) (Table 1, entry 1). After addition of 100 mg of 4 Å MS to the catalytic system, the yield of 2a increased to 23% (Table 1, entry 3). These results show that the 4 Å MS can promote this oxidation reaction to some extent. Considering that H₂O₂ may decompose during the reaction, we employed a speedcontrolled addition system by a syringe pump to realize continuous slow addition. The yields of 2a were significantly increased using a syringe pump. The results are shown in Table 1. The metal catalyst and phase-transfer agent must coexist in this oxidation system (Table 1, entries 5–7). The yield of 2a was raised to 83% in a shorter period (10 h) if Na₂WO₄·2H₂O, PTC, and 4 Å MS were present in the reaction system (Table 1, entry 5). The 4 Å MS was also crucial for achieving high yields of 2a because the yield decreased to 60% in the absence of 4 Å MS (Table 1, entry 4). At lower temperatures such as 50 or 70 °C, this oxidation process was sluggish. We also confirmed that, using 1 mol % of $Na_2WO_4 \cdot 2H_2O$ catalyst, the yield of 2a decreased from 83% to 74% under the same conditions. Thus, the best reaction conditions were elucidated in Table 1, entry 5.

Besides $Na_2WO_4 \cdot 2H_2O$, we also tried to use $Na_2VO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ as catalyst in this catalytic oxidation system. However, the yields were merely 43% and 72%, respectively (Scheme 2, Table 2). The best oxidation catalyst is $Na_2WO_4 \cdot 2H_2O$.

Various benzyl chlorides could also be converted to the corresponding aromatic acids under the same reaction conditions (Scheme 3, Table 3). The substrates bearing electron-withdrawing groups could be more easily oxi-

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Table 1. Oxidation of Benzyl Chloride (10.0 mmol) with $30\%~H_2O_2$ at 90 $^\circ C^a$

entry	H ₂ O ₂ (mL)	PTC (mg)	Na ₂ WO ₄ •2H ₂ O (mg)	4 Å MS (mg)	time (h)	yield ^b (%)
1	3.0	93	66		24	8
2	4.1	93	66		24	15
3	4.1	93	66	100	24	23
4	4.1 ^c	93	66		24	60
5	4.1 ^c	93	66	100	10	83
6	4.1 ^c			100	10	28
7	4.1 ^c	93		100	10	47

^{*a*} Benzyl chloride/H₂O₂/PTC/Na₂WO₄ = 10:36:0.2:0.2 (mole ratio). ^{*b*} Isolated yield. ^{*c*} Added dropwise over 8 h with a syringe pump.

Scheme 2



Table 2. Oxidation of Benzyl Chloride (10.0 mmol) in the Presence of $[CH_3(n-C_8H_{17})_3N]^+HSO_4^-$ (0.2 mmol) and 100 mg 4 Å MS at 90 °C with 30% H₂O₂ Dropwised with a Syringe Pump

	catalyst	time (h)	yield ^a (%)				
	Na ₂ VO ₄ ·2H ₂ O ^b	18	43				
	Na ₂ MoO ₄ ·2H ₂ O ^b	18	72				
	$Na_2WO_4 \cdot 2H_2O^b$	10	83				

^a Isolated yield. ^b 0.2 mmol of catalyst.

Scheme 3

$$\begin{array}{rcl} \text{RCH}_{2}\text{CI} &+ \text{H}_{2}\text{O}_{2} & \\ \hline & & \frac{\text{Na}_{2}\text{WO}_{4} & 2\text{H}_{2}\text{O} & / 4\text{\AA MS}}{\left[\text{CH}_{3}(n\text{-}\text{C}_{8}\text{H}_{17})_{3}\text{N}\right]^{+}\text{HSO}_{4}} & \\ \hline & & \frac{\text{RCO}_{2}\text{H}}{2b \sim 2i} \end{array}$$

2b: R=p-F; 2c: R=p-NO₂; 2d: R=o-CF₃; 2e: R=p-CH₃; 2f: R=p-OMe; 2g: R=p-isopropyl; 2h: R=β-Naphthalene; 2i: R=C₄H₉.

RCH₂Br + H₂O₂
$$\xrightarrow{\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}/4\text{Å}\text{MS}}_{[CH_3(n-C_8\text{H}_{17})_3\text{N}]^+\text{HSO}_4} \xrightarrow{\text{RCO}_2\text{H}}_{90 \ ^{\circ}\text{C}}$$

2j: R=Ph;
2h: R=\beta-Naphthalene

dized to the corresponding aromatic acids than those having electron-donating ones. Thus, many arylaldehydes having electron-donating groups need longer reaction time and large excess of H_2O_2 to achieve higher yields (Table 3). For example, *p*-nitrobenzonic acid **2c** was obtained in 91% yield with 4.1 mL of H_2O_2 , but anisic acid **2f** was formed in only 34% yield with 8.1 mL of H_2O_2 under the same reaction conditions. Steric effects may also play an important role in this reaction because oxidation of *o*-trifluoromethylbenzyl chloride **1d** gave the carboxylic acid **2d** in only 37% yield, along with 32% yield of the corresponding alcohol **3d**. No aliphatic acid could be produced through the oxidation of aliphatic halide

Table 3. Oxidation of Benzyl Chloride and Bromides (10.0 mmol) with 30% H₂O₂ (36.0 or 72.0 mmol) in the Presence of Na₂WO₄·2H₂O (0.2 mmol), [CH₃(*n*-C₈H₁₇)₃N]⁺HSO₄⁻ (0.2 mmol) and 4 Å MS (100 mg) at 90 °C

product	$H_2O_2^a$ (mL)	time (h)	yield ^b (%)	
2b	4.1	10	86	
2c	4.1	10	91	
2d	8.2	18	37	
2e	8.2	18	68	
2f	8.2	18	34	
2g	8.2	18	61	
2h	8.2	18	30	
2i	8.2	18		
2j ^c	4.1	10	88	
$2\mathbf{h}^{e}$	8.2	18	33	

^{*a*} Dropwised with a syringe pump at the speed of 0.5 mL per hour. ^{*b*} Isolated yield. ^{*c*} Benzyl bromide was used. ^{*d*} 32% of *o*-CF₃PhCH₂OH was formed at the same time. ^{*e*} Naphthylmethyl bromide was used.

Scheme 4

$$H_{2}O/Na_{2}WO_{4} \cdot 2H_{2}O$$

$$Ia \qquad H_{2}O/Na_{2}WO_{4} \cdot 2H_{2}O$$

$$H_{2}O/Na_{2}WO_{4} \cdot 2H_{2}O$$

$$H_{2}O/Na_{2}WO_{4} \cdot 2H_{2}O$$

$$H_{2}O/Na_{2}WO_{4} \cdot 2H_{2}O$$

$$H_{2}O/Na_{2}WO_{4} \cdot 2H_{2}O$$

$$\operatorname{ArCH}_{2X} \xrightarrow{\operatorname{H}_{2} \circ / \operatorname{Au}_{2} \circ \circ \circ 4} \operatorname{ArCH}_{2H_{2} \circ \circ \circ 4} \operatorname{ArCH}_{2} \circ \operatorname{ArCOOH} \xrightarrow{\operatorname{ArCOOH}} \operatorname{ArCOOH} \operatorname{ArCOH$$

under the same reaction conditions. The yield for oxidation of benzyl bromide to benzoic acid was slightly higher than that for benzyl chloride (Scheme 3, Table 3).

The oxidation species in the present reaction system is well documented in the literature.^{10,11} The resulting peroxy intermediates are transformed to the desired benzoic acids by a Baeyer–Villiger mechanism.^{5a,f,k} Because the formation of *o*-trifluoromethylbenzyl alcohol **3d** was observed in the reaction, we believe that benzyl chlorides or bromides were first hydrolyzed to the corresponding benzyl alcohols, before being oxidized to the final products.^{11,5a} To confirm this speculation, we carried out the reaction of benzyl chloride **1a** with 5 equiv of water under our catalytic system at 90 °C and found that 886 mg (82%) of benzyl alcohol **3a** was indeed formed (Scheme 4). On the basis of these results, we propose the plausible mechanism of the oxidation process shown above in Scheme 4.

In conclusion, we have developed a useful, practical, and eco-safer protocol for the preparation of aromatic acids from benzyl halides. Judging from the conditions employed, this oxidation method showed have great prospects in industrial applications. Efforts to elucidate the scope and limitations of this oxidation system are underway.

Experimental Section

General Methods and Materials. Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a Bruker

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AM-90 spectrometer or a Bruker AM-300 in CDCl₃ with tetramethylsilane (TMS) as internal standard; *J* values are given in Hz. Mass spectra were recorded on an HP-5989 instrument, and HRMS was measured on a Finnigan MA+ mass spectrometer. Organic solvents were dried by standard methods when necessary. Some of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. The preparation of methyltri-*n*-octylammonium hydrogensulfate (PTC) is according to the literature.^{3a,12} All reactions were monitored by TLC with Huanghai GF₂₅₄ silica gel coated plates. Flash column chromatography was carried out on 300-400 mesh silica gel.

Preparation of Benzoic Acid (2a). To the reaction mixture of benzyl chloride 1a (1.27 g, 10.0 mmol), Na₂WO₄·2H₂O (66 mg, 0.2 mmol), PTC (93 mg, 0.2 mmol), and 4 Å MS (100 mg) was added 30% hydrogen peroxide solution (4.1 mL, 36 mmol) dropwise at a speed of 0.5 mL/h by means of a syringe pump over 8 h at 90 °C with stirring vigorously. After being stirred for another 2 h at 90 °C, the mixture was cooled to room temperature. The aqueous layer was extracted with 10.0 mL of EtOAc three times. The combined organic layer was washed with 10 mL of saturated aqueous Na₂S₂O₄ and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure. After recrystallization from hexane, 2a was obtained as a white solid (1.07 g, 83%). Mp: 121–122 °C (lit.^{13a} mp 121–123 °C). ¹H NMR (CDCl₃, 90 MHz): δ 7.34–7.61 (3H, m, År), 8.17 (2H, d, J=6.3 Hz, År), 8.90–9.83 (1H, br s, OH). ¹³C NMR (CDCl₃, 75 MHz): δ 128.50, 129.42, 130.23, 133.79, 172.28. MS (EI) *m*/*z* (rel int): 122 (89.94, M^+), 105 (100, $M^+ - 17$), 77 (81.50, $M^+ - 45$), 74 (9.89, $M^+-48),\,51$ (36.16, $M^+-71),\,50$ (25.52, $M^+-72).$ Anal. Calcd: C, 68.84; H, 4.95. Found: C, 68.35; H, 5.01.

Benzyl bromide was oxidized to **2a** in the same manner as that described above, but the yield of **2a** can reach 88%.

Preparation of 4-Fluorobenzoic Acid (2b). This compound was prepared in the same manner as that described above as a white solid (1.03 g, 86%). Mp: 184–186 °C (lit.^{13b} mp 185.4–187.2 °C). ¹H NMR (CDCl₃, 90 MHz): δ 7.16 (1H, dd, J = 8.9, 8.9 Hz, Ar), 7.36 (1H, dd, J = 8.9, 8.9 Hz, Ar), 8.15 (1H, dd, J = 8.9, 5.4 Hz, Ar), 8.24 (1H, dd, J = 8.9, 5.4 Hz, Ar), 8.40–9.26 (1H, br s, OH). ¹³C NMR (CDCl₃, 75 MHz): δ 115.74 (d, J_{C-F} = 21.975 Hz), 125.65, 132.88 (d, J_{C-F} = 9.45 Hz), 166.4 (d, J_{C-F} = 253.5 Hz), 170.91. Anal. Calcd: C, 60.01; H, 3.40. Found: C, 59.25; H, 3.61.

Preparation of 4-Nitrobenzoic Acid (2c). This compound was prepared in the same manner as that described above as a slightly yellow solid (1.52 g, 91%). Mp: 241–243 °C (recrystallization from EtOAc) (lit.^{13c} mp 243.5–244.5 °C). ¹H NMR (D₃CCOCD₃, 90 MHz): δ 8.26 (2H, d, *J* = 10.8 Hz, Ar), 8.39 (2H, d, *J* = 10.8 Hz, Ar), 3.65–3.96 (1H, br s, OH). ¹³C NMR (D₃CCOCD₃, 75 MHz): δ 124.42, 131.72, 137.22, 151.50, 166.27. Anal. Calcd: C, 50.31; H, 3.02, N, 8.38. Found: C, 50.23; H, 3.08; N, 8.40.

Preparation of 2-Trifluoromethylbenzoic Acid (2d). This compound was prepared in the same manner as that described above. However, 8.2 mL (72 mmol) of H_2O_2 was added dropwise over 16 h into the substrate 1d, and the products 2d and 3d

were isolated by silica gel column chromatography (eluent: EtOAc/petroleum ether = 1/10). **2d** (a white solid, 730 mg, 37%). Mp: 108–109 °C (lit.^{13d} mp 108–109.5 °C). ¹H NMR (CDCl₃, 300 MHz): δ 7.64 (1H, dd, J = 7.8, 7.8 Hz, Ar), 7.89 (1H, d, J = 7.8 Hz, Ar), 8.32 (1H, d, J = 7.8 Hz, Ar), 8.40 (1H, s, Ar), 10.6 (1H, br s, OH). ¹³C NMR (CDCl₃, 75 MHz): δ 123.60 (q, J_{C-F} = 270.75 Hz), 127.21 (q, J_{C-F} = 3.75 Hz), 129.28, 130.20, 130.43 (q, J_{C-F} = 3.60 Hz), 131.37 (q, J_{C-F} = 32.92 Hz), 133.41, 171.04 (q, J_{C-F} = 2.25 Hz). Anal. Calcd: C, 50.54; H, 2.65. Found: C, 50.45; H, 2.73.

3d (a colorless oil, 563 mg, 32%). Bp: 90 °C/20 mmHg. ¹H NMR (CDCl₃, 90 MHz): δ 1.72–2.16 (1H, br s, OH), 4.82 (2H, s, CH₂), 7.43–7.79 (4H, m, Ar). ¹³C NMR (CDCl₃, 75 MHz): δ 64.54, 123.54 (q, $J_{C-F} = 2.85$ Hz), 124.14 (q, $J_{C-F} = 202.95$ Hz), 124.38 (q, $J_{C-F} = 2.85$ Hz), 128.98, 130.04, 130.93 (q, $J_{C-F} = 24.08$ Hz), 141.75. MS (EI) *m*/*z* (rel int): 176 (59.34, M⁺), 175 (30.22, M⁺ – 1), 127 (100, M⁺ – 49), 107 (92.51, M⁺ – 69), 80 (20.52, M⁺ – 96), 77 (37.22, M⁺ – 99). HRMS (EI): *m*/*z* 176.0443 (M⁺), C₈H₇F₃O requires M 176.0449.

Preparation of Toluic Acid (**2e**). This compound was prepared in the same manner as that described for the preparation of **2d** (a white solid, 0.92 g, 68%). Mp: 180–181 °C (lit.^{13e} mp 182–183 °C). ¹H NMR (CDCl₃, 90 MHz): δ 2.45 (3H, s, CH₃), 7.28 (2H, d, J = 8.1 Hz, Ar), 8.04 (2H, d, J = 8.1 Hz, Ar), 8.30–9.96 (1H, br s, OH). ¹³C NMR (CDCl₃, 75 MHz): δ 27.80, 126.64, 129.23, 130.29, 144.66, 172.37. Anal. Calcd: C, 70.58; H, 5.92. Found: C, 70.23; H, 5.97.

Preparation of Anisic Acid (**2f**). This compound was prepared in the same manner as that described in the preparation of **2d** (a white solid, 0.52 g, 34%). Mp: 184–185 °C (lit.^{13f} mp 186–187 °C). ¹H NMR (CDCl₃, 90 MHz): δ 3.90 (3H, s, CH₃), 6.94 (2H, d, *J* = 8.1 Hz, Ar), 8.08 (2H, d, *J* = 8.1 Hz, Ar). ¹³C NMR (CDCl₃, 75 MHz): δ 55.50, 113.78, 121.70, 132.38, 164.08, 171.56. Anal. Calcd: C, 63.15; H, 5.30. Found: C, 63.10; H, 5.21.

Preparation of 4-Isopropylbenzoic Acid (2g). This compound was prepared in the same manner as that described in the preparation of **2d** (a white solid, 1.0 g, 61%). Mp: 118–120 °C (lit.^{13g} mp 118–119 °C). ¹H NMR (CDCl₃, 300 MHz): δ 1.28 (6H, d, J = 8.0 Hz, CH₃), 2.99 (1H, m, Ar), 7.33 (2H, d, J = 8.2 Hz, Ar), 8.05 (2H, d, J = 8.2 Hz, Ar). ¹³C NMR (CDCl₃, 75 MHz): δ 23.65, 34.35, 126.61, 127.01, 130.44, 155.37, 172.64. Anal. Calcd: C, 73.15; H, 7.37. Found: C, 73.10; H, 7.34.

Preparation of 2-Naphthoic Acid (2h). This compound was prepared in the same manner as that described in the preparation of **2d** (white solid, 516 mg, 30% yield). Mp: 185–187 °C (lit.^{13h} mp 185–186 °C). ¹H NMR (CDCl₃, 90 MHz): δ 5.27–6.80 (1H, br s, OH), 7.39–7.78 (2H, m, Ar), 7.78–8.49 (5H, m, Ar), 8.73 (1H, s, Ar). ¹³C NMR (CDCl₃, 75 MHz): δ 125.42, 126.80, 127.84, 128.36, 128.69, 129.57, 130.91, 132.19, 132.48, 136.00, 171.93. Anal. Calcd for: C, 76.73; H, 4.68. Found: C, 76.64; H, 4.65.

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Supporting Information Available: ¹³C NMR spectra of **2a–h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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