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OXIDATION OF BENZALDEHYDES TO BENZOATE ESTERS USING HOUSEHOLD BLEACH AND SODIUM IODIDE IN ALCOHOL SOLVENTS

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GRAPHICAL ABSTRACT



Abstract Various substituted benzaldehydes were converted into benzoate esters with household bleach and sodium iodide in an alcohol solvent. The reaction works best with methanol. Only 4-chlorobenzaldehyde, 3-nitrobenzaldehyde, and 4-nitrobenzaldehyde reacted completely with 1-propanol under these conditions.

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications[®] for the following free supplemental resource(s): Full experimental and spectral details.]

Keywords Benzaldehydes; bleach; esters; iodide; oxidation

INTRODUCTION

Previously, we reported on iodination of hydroxy- and methoxy-substituted benzaldehydes using iodine and silver nitrate^[1,2] and using iodine and periodic acid.^[2] Other authors,^[3,4] have reported that vanillin and similar compounds may be iodinated using sodium hypochlorite and either sodium iodide or potassium iodide in methanol. We reacted 4-methoxybenzaldehyde, **1a**, with sodium hypochlorite and sodium iodide in methanol, **2a**, and discovered no ring iodination occurred. Instead, the methyl ester, methyl 4-methoxybenzoate, **3a**, was isolated in 59% yield. The reaction is shown in Scheme 1.

The conditions of this reaction were modified systematically, to see if the yield of 3a could be improved. The results are shown in Table I.

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Scheme 1. Reaction of 4-methoxybenzaldehyde with bleach and sodium iodide in methanol.

As can be seen be seen in entries 1 and 2, both sodium iodide and bleach are required for the esterification to occur. It had been previously reported^[5] that esters could be formed from benzaldehydes using 1–2 equivalents of bleach and acetic acid in methanol. As shown in entry 3, under these conditions we isolated an approximately 3:1 mixture (by NMR) of **1a** and 3-chloro-4-methoxybenzaldehyde, with no indication of ester products formed. Modifying our original procedure by doubling the amount of either sodium iodide or bleach (entries 5 and 6) increased the yield some, but doubling both (entry 7) increased the yield to 79%. Increasing the amount of sodium iodide further did not increase the yield (entry 8), nor did increasing the reaction time (entry 9). Entry 10 was tried to see if sodium iodide might have a catalytic role (oxidized to iodine and subsequently reduced back to iodide), but a 3:1 mixture of **1a**:**3a** was formed after 17 h of stirring. Using 3 equivalents each of iodine and potassium carbonate in methanol^[6] under our reaction conditions yielded a 5:1 mixture of **1a**:**3a**.

After optimizing the reaction conditions, we submitted various substituted benzaldehydes to these conditions. Other alcohols were also tried. This is illustrated in Scheme 2. The successful reactions are shown in Table 2.

Most benzaldehydes reacted with methanol to form methyl esters in yields of around 80%. The isolated solid products were pure (no evidence of aldehyde or alcohol starting materials, or byproducts, by proton NMR), and did not require

Entry	Equiv. of 1a	Equiv. of NaI	Equiv. of NaOCl	Other	Yield (%) of ester 3a or other result
1	1	1	0	0	NAR ^a
2	1	0	1	0	NAR
3	1	0	2	2 acetic acid	Mixture of 1a and
					3-chloro-4-methoxybenzaldehyde (3:1)
4	1	1	1	0	58%
5	1	2	1	0	62%
6	1	1	2	0	67%
7	1	2	2	0	79%
8	1	5	2	0	70%
9	1	2	2	Stir 17h	74%
10	1	0.2	2	Stir 17h	1a and 3a (7:3)
11	1	0	0	3 I_2 and 3 K_2CO_3	1a and 3a (5:1)

Table 1. Optimization of reaction conditions with 4-methoxybenzaldehyde (1a) and methanol (2a)

"NAR means no apparent reaction.



Scheme 2. General reaction of benzaldehydes with bleach and sodium iodide in alcohol solvents.

further purification. However, 2-, 3-, and 4-hydroxybenzaldehydes formed mixtures of mono- and di-iodinated products, even when using 1 equivalent of sodium iodide and sodium hypochlorite. 3,4-Dimethoxybenzaldehyde cleanly formed the methyl ester, with no ring iodination. This is in contrast to what we reported using silver nitrate and iodine, where only ring iodination was observed.^[2]

Attempts to use other alcohols were not as successful. These results are shown in Table 3.

The products formed when using ethanol and 1-propanol as solvents with **1a** were contaminated with starting aldehyde: the reaction apparently did not go to completion in these solvents. No ester was detected in the reaction of **1a** with 2-propanol. The use of ethanol and 2-propanol also led to formation of some iodoform, which contaminated the ester products. This is not unexpected, because bleach readily promotes the iodoform reaction, and basic solutions of iodine can also oxidize primary and secondary alcohols to carbonyl compounds.^[7] The reaction of benzaldehyde with 1-propanol formed mostly ester, but there was still unreacted benzaldehyde. The only reactions that produced pure ester products were using 4-chlorobenzaldehyde, 3-nitrobenzaldehyde, and 4-nitrobenzaldehyde with 1-propanol. Other authors ^[6,8,9] have proposed that hemiacetals are intermediates in similar oxidations using hypochlorite. Perhaps only the carbonyls of these aldehydes form significant amounts of the hemiacetals with the larger alcohols, which can then be oxidized to esters under these conditions.

 Table 2. Successful reactions and yields of ester products

Aldehyde	G	Alcohol	R	Ester	Yield (%) of ester
1a 1b 1c 1d 1e 1f 1g	4-CH ₃ O 4-CH ₃ 4-Cl 3-NO ₂ 4-NO ₂ 3,4-(CH ₃ O) ₂ H	2a 2a 2a 2a 2a 2a 2a 2a	$\begin{array}{c} CH_3\\ CH_3\\ CH_3\\ CH_3\\ CH_3\\ CH_3\\ CH_3\\ CH_3\\ CH_3\end{array}$	3a 3b 3c 3d 3e 3f 3g	79 86 85 76 84 73 80
1d 1e 1c	3-NO ₂ 4-NO ₂ 4-Cl	2b 2b 2b	$\begin{array}{c} CH_3CH_2CH_2\\ CH_3CH_2CH_2\\ CH_3CH_2CH_2\end{array}$	3h 3i 3j	74 81 81

Aldehyde	G	Alcohol	Results
1a	4-CH ₃ O	Ethanol	Iodoform (0.58 g) and an oil (0.82 g, which was a 7:1 mixture of 1a and ester)
1a	4-CH ₃ O	1-Propanol	0.91 g of an oil, which was a 6:1 mixture 1a and ester
1a	4-CH ₃ O	2-Propanol	Iodoform (1.004 g) and an oil, which was 1a (0.86 g, 91% recovery)
1g	4-H	1-Propanol	0.82 g of an oil, which was a 1:10 mixture of 1g and ester
1e	4-NO ₂	Ethanol	1.33 g of solid, which was a 10:1 mixture of ester and iodoform
1e	4-NO ₂	2-Propanol	1.13 g of solid, which was a 3:5:1 mixture of 1e , ester, and iodoform

Table 3. Results of reactions of ethanol, 1-propanol, or 2-propanol (30 mL) and various aldehydes (7 mmol), with 2 equivalents each of sodium iodide and sodium hypochlorite

In conclusion, a number of simple benzaldehydes can be oxidized to methyl esters using sodium iodide and household bleach in methanol in good yields. The procedure and product isolation are simple for solid esters, and the esters are pure, with no unreacted benzaldehyde, as determined by proton NMR spectroscopy. In addition, 4-chlorobenzaldehyde, 3-nitrobenzaldehyde, and 4-nitrobenzaldehyde also form pure ester products with 1-propanol.

EXPERIMENTAL

Melting ranges were recorded using a MelTemp apparatus and are reported in °C. NMR spectra were recorded on a Bruker DPX-300 or on an Anasazi EFT-upgraded Varian EM-360, using CDC1₃ or dimethylsulfoxide (DMSO-d₆) as a solvent.

4-Methoxybenzaldehyde, 1a (0.95 g, 7.0 mmol), sodium iodide (2.10 g, 14.0 mmol), and methanol, **2a** (30 mL) were added to a 250-mL Erlenmeyer flask. The mixture was stirred until the solids dissolved and then stirred in an ice-water bath for 10 min. Commercial household bleach (either 22 mL of a 5.25% solution or 15 mL of an 8% solution, which was titrated with standard sodium thiosulfate solution to determine the actual concentration of sodium hypochlorite) (14 mmol) was added dropwise over 20 min to the cooled reaction mixture: The solution turned brown with the addition of bleach. The ice bath was removed, and the reaction mixture was stirred for 1 h. Enough sodium thiosulfate solution (either 5% or 10%) was added to discharge the iodine color. The solution was diluted with 100 ml of water and allowed to stand in an ice bath until precipitation of the solid product was complete. The solid was filtered by suction, washed with water, and allowed to dry. Compound **3a** was a white solid, melting range: $46-47 \,^{\circ}$ C (literature $49 \,^{\circ}$ C^[10]). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.00 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 9.0 Hz, Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H). ¹³C NMR (75.5 MHz, CDCl₃), δ (ppm): 166.9, 163.3, 131.6, 122.6, 113.6, 55.4, 51.9. The spectral data agreed with that in the literature.[11]

In those cases where the product did not solidify upon cooling, the reaction mixture was extracted with dichloromethane $(2 \times 25 \text{ mL})$. The combined dichloromethane extracts were washed with water and saturated sodium chloride solution,

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and dried over sodium sulfate. The solvent was removed under reduced pressure. For product mixtures, the integrations of the aldehyde protons and the ester $O-CH_2$ or O-CH protons were used to obtain the product ratios. If iodoform was present in a mixture, it was quantitated by its distinctive NMR signal at 4.90 ppm in CDCl₃.

SUPPORTING INFORMATION

Full experimental details, melting ranges, and ¹H and ¹³C NMR spectral data for compounds **3b–j** can be found via the Supplementary Content section of this article's Web page.

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