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Tanveer Mohammad Ali Shaikh [a] , Lourdusamy Emmanuvel [a] & Arumugam Sudalai [a]

[a] National Chemical Laboratory, Chemical Engineering and Process Development Division, Pune, Maharastra, India

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$NaIO_4$/LiBr-Mediated Direct Conversion of Benzylic Alcohols and Aromatic Aldehydes to Aromatic Esters

Tanveer Mohammad Ali Shaikh, Lourdusamy Emmanuvel,
and Arumugam Sudalai
National Chemical Laboratory, Chemical Engineering and Process
Development Division, Pune, Maharastra, India

Abstract: Aromatic aldehydes or benzylic alcohols are directly converted to the corresponding aromatic esters in high yields on treatment with methanol or ethanol mediated by sodium metaperiodate ($NaIO_4$)/LiBr in an acidic medium.

Keywords: aromatic ester, benazaldehyde, benzyl alcohol, lithium bromide, sodium metaperiodate

The direct conversion of aldehydes or alcohols to the corresponding carboxylic esters is often required in organic synthesis, particularly in the synthesis of natural products.[1] The conventional method for the synthesis of carboxylic esters involves oxidation of aldehydes to carboxylic acids followed by esterification with alcohols catalyzed by either acid or base. In contrast, the direct method of conversion of alcohols or aldehydes to carboxylic esters holds promise in organic synthesis because it minimizes the number of steps. Such transformation of aldehydes directly into esters has

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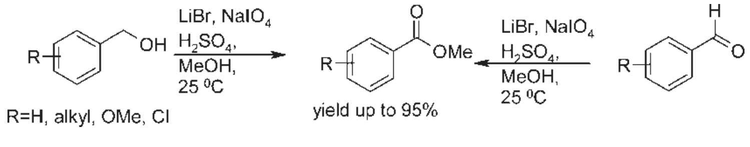
Address correspondence to Arumugam Sudalai, National Chemical Laboratory, Chemical Engineering and Process Development Division, Dr. Homi Bhabha Road, Pune 411008, Maharastra, India. E-mail: a.sudalai@ncl.res.in

been achieved using a variety of reagents such as V_2O_5/H_2O_2,[2] oxone®,[3] $DMSO/Ac_2O$,[4] $Br_2/NaHCO_3$,[5] O_3/KOH,[6] pyridinium hydrobromide perbromide,[7] pyridinium dichromate,[8] electrochemical methods,[9] TMSOTf/NBS/AIBN,[10] $S \cdot SnO_2/SBA\text{-}1\text{-}H_2O_2$,[11] and more recently acetone cyanohydrin.[12] Also, the direct conversion of alcohols into esters has been achieved using oxone®/NaCl,[13] $Ca(OCl)_2$,[14] pyridinium hydrobromide perbromide,[7] $NaBrO_3/NaHSO_3$,[15] $NaBrO_2/AcOH$,[16] $PhI(OAc)_2$,[17] and H_2O_2/Br_2.[18] Unfortunately, many of these procedures often require a large excess of reagents, expensive catalysts, transition metals, dry solvents, stringent reaction conditions, photochemical methods, and so on. Moreover, the formation of carboxylic acids due to the over oxidation of aldehydes further complicates the reaction and results in diminished yield of the esters.

Recently, we reported[19] that $NaIO_4$-mediated oxidation of alkylarenes led to the high-yield preparation of benzoic acids, formed via the oxidation of their respective benzyl alcohols and aldehydes when the reaction was carried out in water. In this regard, we envisioned that replacing water with alcohol should result in the formation of esters. In this communication, we report that the $NaIO_4$-LiBr-H^+ combination oxidizes benzylic alcohols or aromatic aldehydes directly to the corresponding aromatic esters in high yields (Scheme 1).

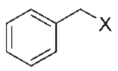
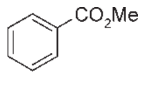
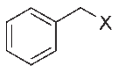
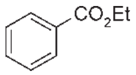
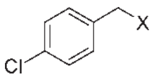
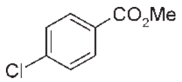
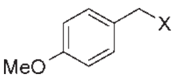
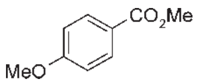
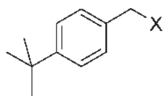
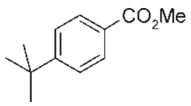
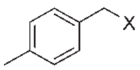
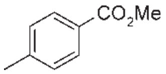
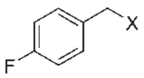
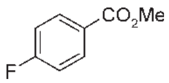
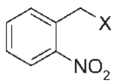
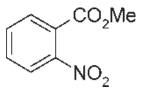
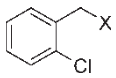
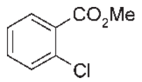
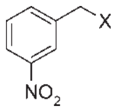
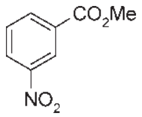
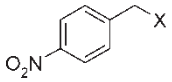
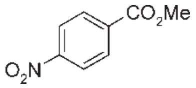
To establish the scope of this reaction, a number of aromatic aldehydes and benzylic alcohols were subjected to oxidation, and the results are given in Table 1.

As can be seen from Table 1, both aromatic aldehydes and benzylic alcohols with electron-donating as well as electron-withdrawing substituents on the nucleus underwent oxidative esterification smoothly to give their corresponding aromatic esters in 71–95% yields. In the case of substrates with electron-donating groups, the reaction proceeded at 25°C whereas the substrates with electron-withdrawing groups, except 4-chloro aromatics (entry 3), required higher temperatures (65°C) to achieve excellent conversions. For 4-methoxy-benzyl alcohol, the oxidative esterification occurred along with nuclear bromination when 2 molar equivalents of LiBr were used (entry 4). We also observed that use of substoichiometric amounts of $NaIO_4$ (25–40 mol%) resulted in poor yields of esters (<40%).



Scheme 1. $NaIO_4$/LiBr-mediated direct oxidative esterification of benzylic alcohol and benzaldehydes.

Table 1. Direct conversion of benzylic alcohols or aldehydes to aromatic esters[a]

			Product yield[b]	
Entry	Substrate	Product	X = OH	X = O
1			89	98
2[c]			78	82
3			86	91
4			77[d]	85
5			80	87
6			73	85
7			77	83
8[e]			78	80
9[e]			71	78
10[e]			73	79
11[e]			80	82

[a] Alcohol or aldehyde (3 mmol), $NaIO_4$ (3 mmol), LiBr (3 mmol), conc. H_2SO_4 (1 mL), methanol (9 mL), 25°C, 18 h.

[b] After purification by column chromatography.

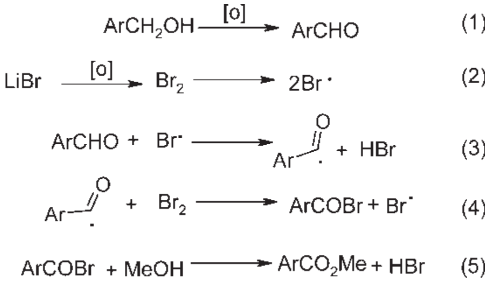
[c] Ethanol was used as the solvent.

[d] Yield of the methyl 3-bromo-4-methoxybenzoate when two equivalents of LiBr are used.

[e] Reaction done at 65°C with aq. H_2SO_4 (0.85 N, 1 mL).

Among the several solvent combinations screened, a mixture of MeOH/H_2O (9:1, 10 ml) gave the highest yield of esters. Control experiments have proved that both $NaIO_4$ and LiBr are needed to produce esters. Ethanol was also found to give ethyl esters (entry 2), whereas other alcohols such as 2-propanol and benzyl alcohol failed to give their respective esters, probably because of steric hindrance. Aliphatic alcohols or aldehydes were found to be inactive under the reaction conditions, which may be a limitation of this process. Replacing LiBr with other halide sources such as tetrabutylammonium bromide or NaBr also brought about this conversion with comparable yield, whereas KI and NaCl failed.

Based on the observations that no traces of acetal or carboxylic acid were identified in the present study as well as from our earlier work on $NaIO_4$/LiBr-mediated reactions,[19] a probable mechanism[18] for the oxidative esterification of aromatic aldehydes and benzylic alcohols is given in Scheme 2. Initially, benzylic alcohols are oxidized to the corresponding aromatic aldehydes [Eq.(1)], which subsequently undergo oxidative esterification with methanol via a radical pathway as shown in Eqs. (2–5).



Scheme 2. Proposed radical pathway for the direct esterification of aromatic aldehydes and benzylic alcohols.

In conclusion, we have developed a new oxidative procedure for the direct conversion of both activated and deactivated benzylic alcohols or aromatic aldehydes to the corresponding aromatic esters in high yields using $NaIO_4$/LiBr/H^+ as the reagent system.

EXPERIMENTAL

Reagents and solvents were commercially available and were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer. Column chromatography was performed on silica gel (60–120 mesh).

Typical Experimental Procedure

Lithium bromide (3 mmol) to a 50-ml round-bottom flask charged with aromatic aldehyde or benzylic alcohol (3 mmol), sodium metaperiodate (3 mmol), and conc. H_2SO_4 (1 mL) in methanol (9 ml) was added at 25°C. The reaction mixture was stirred for 18 h, and then the solvent was removed under reduced pressure. The residue was extracted with ethyl acetate, and the organic phase was washed with water, saturated and $Na_2S_2O_3$, and brine; dried over anhydrous sodium sulphate; and concentrated under reduced pressure. The crude ester was purified over silica gel (60–120 mesh) by column chromatography using hexane/EtOAc (19:1) as eluent.

Data

Methyl 4-fluorobenzoate: mp of methyl 4-fluorobenzoate = 89–90°C. ^1H NMR ($CDCl_3$) δ 3.91 (s, 3H), δ 7.06–7.15 (dd, 2H, $J = 6$ Hz), δ 8.02–8.09 (dd, 2H, $J = 6$ Hz). ^{13}C NMR ($CDCl_3$) 51.90, 115.07, 115.50, 126.27, 131.86, 132.04, 163.06, 165.82, 168.11.

Methyl 4-*tert*-butylbenzoate: ^1H NMR ($CDCl_3$) δ 1.34 (s, 9H), δ 3.90 (s, 3H), δ 7.43–7.47 (dd, 2H, $J = 8$ Hz), δ 7.95–7.99 (dd, 2H, $J = 8$ Hz). ^{13}C NMR ($CDCl_3$) 31.09, 35.04, 51.89, 125.25, 127.31, 129.38, 156.42, 167.02

Methyl benzoate: ^1H NMR ($CDCl_3$) δ 3.92 (s, 3H), δ 7.39–7.56 (m, 3H), δ 8.01–8.06 (dd, 2H, $J = 8$ Hz). ^{13}C NMR ($CDCl^3$) 52, 128.30, 129.53, 130.21, 132.82, 166.99.

Methyl 4-nitrobenzoate: mp of methyl 4-fluorobenzoate = 89–90°C. ^1H NMR ($CDCl_3$) δ 3.99 (s, 3H), δ 8.19–8.32 (m, 4H). ^{13}C NMR ($CDCl_3$) 52.79, 123.50, 130.68, 135.51, 150.51, 165.10.

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