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AN IMPROVED PROTOCOL FOR SYNTHESIS OF IODOHYDROXYBENZALDEHYDE USING IODINE AND IODIC ACID

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ABSTRACT

Treatment of iodine and iodic acid on substituted hydroxybenzaldehydes affords respective iodo hydroxybenzaldehydes in high yield. The notable advantage of this protocol is no use of catalyst, mild reaction conditions, short time and simple operation with high yield of the products.

Key words: Iodine, Iodic acid, Iodohydroxybenzaldehyde.

INTRODUCTION

Iodoaromatic compounds have been employed in organic synthesis[1], because they can be readily functionalized through carbon-carbon bond formation of diarenes, ethylenic or acetylenic condensation using transition metal or carbon-hetero atom bonds[2]. The iodination of aromatic compounds has been the subject of numerous studies due to their potential ability as intermediates in organic synthesis and also as bacterial and fungicidal agents[3]. The direct introduction of iodine into aromatic molecules under mild conditions needs some additive to activate the low reactivity of iodine. In recent years, the direct iodination methods have been intensively developed by using iodonium donating systems, such as iodine-nitrogen dioxide[4], iodine-F-TEDA (1-chloromethyl-4-fluro-1,4-diazoniabicyclo[2,2,2] octane bis tetra fluroborate)[5], NIS (N-iodosuccinamide)[6], iodine-diiodine pentaoxide[7], iodine-mercury (II) oxide[8], iodine monochloride[9], bis (pyridine) iodonium (I), tetrafluroborate- CF_3SO_3H[10], NIS- CF_3SO_3H[11], iodine silver sulphate[11], iodine-mercury salt[13] and NaOCl - NaI[14]. However, most of these methods require hazardous or toxic and costly reagent or high reaction temperatures and for long reaction time.

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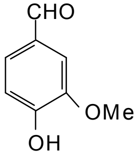
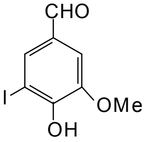
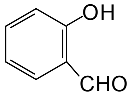
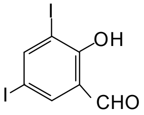
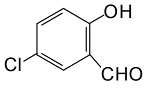
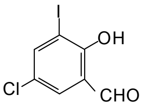
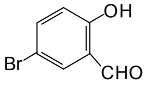
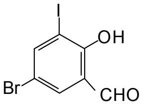
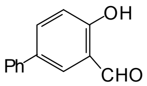
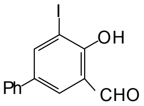
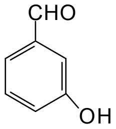
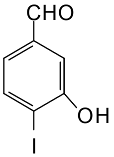
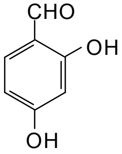
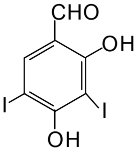
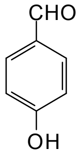
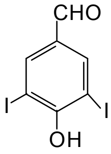
We report here a normal method for iodination of benzaldehydes using selective iodinating agent, iodine and iodic acid. The combination of iodine and iodic acid has been found to be excellent reagent for the efficient iodination of aromatic benzaldehydes **(Scheme 1)**. The notable advantage of this protocol is no use of catalyst, mild reaction conditions, short time and simple operation with high yield using cheap and commonly available reagents.

In order to generalize the iodination reaction, a series of different substituted benzaldehydes were submitted to reaction with iodine and iodic acid in the ethyl alcohol. The excess of iodine was neutralized by treatment with saturated sodium thiosulphate solution. The results are outlined in Table 1.

Table 1. Physical and analytical data of iodoaldehydes

S. No.	Substrate	Product	M. P. (°C)	Yield (%)	% Halogen found (Calcd.)	^{1}H NMR (δ values)
1.			183 (185)[15]	75	44.98 (45.68)	9.90 (s, 1H, CHO) 8.06 (s, 1H, Ar-OH) 7.34 (s, 1H, 2Ar-H) 7.58 (s, 1H, 6Ar-H) 4.80 (s, 3H, OCH_3)
2.			110 (110)[16]	87	68.12 (67.91)	11.82 (s, 1H, Ar-OH) 9.97 (s, 1H, CHO) 8.13 (s, 1H, 4Ar-H) 8.01 (s, 1H, 6Ar-H)
3.			76 (78)[17]	85	57.43 (57.62)	11.74 (s, 1H, Ar-OH) 9.73 (s, 1H, CHO) 8.20 (s, 1H, 4Ar-H) 7.64 (s, 1H, 6Ar-H)
4.			80 (81)[18]	68	63.48 (63.10)	11.68 (s, 1H, Ar-OH) 9.82 (s, 1H, CHO) 7.92 (s, 1H, 4Ar-H) 7.80 (s, 1H, 6Ar-H)

S. No.	Substrate	Product	M. P. (°C)	Yield (%)	% Halogen found (Calcd.)	^{1}H NMR (δ values)
5.			135 (--)	57	40.02 (39.19)	13.01 (s, 1H, Ar-OH) 9.83 (s, 1H, CHO) 7.32-7.97(m,7H, Ar-H)
6.			182 (--)	78	51.80 (51.20)	9.89 (s, 1H, CHO) 8.23 (s, 1H, Ar-OH) 7.05-7.67(m,3H, Ar-H)
7.			172 (--)	70	64.89 (65.12)	11.85 (s, 1H, Ar-OH) 10.08 (s, 1H, CHO) 7.86 (s, 1H, 6Ar-H)
8.			194 (193)[18]	75	67.54 (67.91)	9.87 (s, 1H, CHO) 8.15 (s, 1H, Ar-OH) 8.02 (s, 2H, 2,6Ar-H)

EXPERIMENTAL

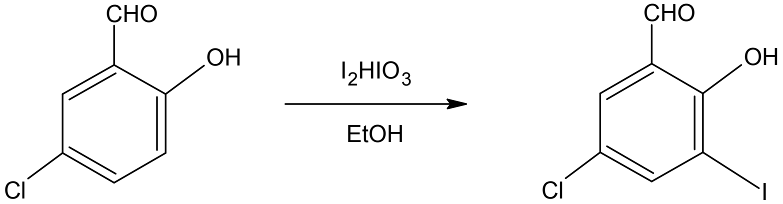
All melting points are taken in open capillaries and are uncorrected. The IR spectra in KBr were recorded on Perkin-Elmer 157 spectrophotometer (ν_{max} in cm^{-1}) and ^{1}H NMR spectra on Bruker WM 400 FTMHz NMR instrument using CDCl$_3$ as reference (chemical shifts in δ ppm). The homogeneity of the compounds was ascertained by TLC. The spots were developed in iodine chamber.

Synthesis of 2-hydroxy-3-iodo-5-chlorobenzaldehyde (3)

A mixture of 2-hydroxy-5-chlorobenzaldehyde (0.05 m) and iodine crystals (0.02 m) were dissolved in ethyl alcohol (20 mL). Reaction mixture was heated to about 35°C temperature and iodic acid (0.01 m) in water (2 mL) was added with stirring for 2 hrs. The reaction mixture was diluted with water; unreacted iodine was decomposed by adding saturated solution of sodium thiosulphate. Solid gets separated, which was filtered and washed with water and recrystallized from ethyl alcohol to get **(3).**

Similarly, other iodo hydroxybenzaldehydes were synthesized by following above procedure.

For the synthesis of diiodobenzaldehydes, excess of iodine was used.



Scheme I

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