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A Direct Transformation of Aryl Aldehydes to Benzyl Iodides Via Reductive Iodination

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ABSTRACT: A facile transformation of aryl aldehydes to benzyl iodides through one-pot reductive iodination is reported. This protocol displays remarkable functional group tolerance and the title compound was obtained in good to excellent yield.

Key words: Benzyl iodides, Triethylsilane, Reductive iodination

INTRODUCTION

Benzyl iodides are important subunit in organic synthesis. They are found to have broad applications in fields of fine chemicals, pharmaceuticals, medicinal chemistry and drug discovery.[1–4] Although they possess numerous synthetic utilities, it has been primarily used to form carbon–carbon and carbon–heteroatom bonds. Unlike other halides, benzyl iodides are prepared freshly before use due to their low stability. Evidently, many synthetic protocols have been developed for the synthesis of benzyl iodides, however, most of the methods describe their preparation from the corresponding alcohol.[5] Moreover, the projected benzyl iodide synthesis from aryl aldehyde involves two steps, proceeds via the intermediacy of benzyl alcohol. Conversely, it can be obtained in a single step by employing reductive iodination.[6] Despite of its importance, this protocol has been less explored and thus found limited exploitation in synthesis.

Over the past few decades, organosilanes are emerged as popular reagents in synthetic chemistry.[7] In the past, chlorotriethylsilane, dichloromethylsilane and polymethylhydrosiloxane were used for the reductive iodination, however, they had limited substrate scope.[6a–d] Also, few of these methods suffer from tedious work up procedures, harsh conditions and long reaction time. Triethylsilane (Et_3SiH) is another versatile and commercially available reagent utilized for many transformations, for example, the reduction of carbonyl derivative.[8] Consequently, we planned to develop one-pot strategy to access benzyl iodide from aryl aldehyde using triethylsilane. Herein, we disclose a facile and convenient reductive iodination of aryl aldehydes using Et_3SiH and trifluoromethanesulfonic acid (TfOH) in presence of sodium iodide.

EXPERIMENTAL

All reagents were purchased from commercial suppliers and were used without purification. Melting points were determined in Buchi B-545 melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance and Varian 400 & 300 NMR MHz spectrometers in DMSO-d_6 & $CDCl_3$ solution using TMS as an internal reference and ^{13}C NMR spectra were recorded on 100 & 75 MHz. Mass spectra were recorded on GC-MS using 230–400 mesh silica gel.

Typical Experimental Procedure for the Preparation of Benzyl Iodides

To an ice-cold solution of 4-bromo benzaldehyde **1a** (0.18 g, 1 mmol) in CH_3CN/DME (5 mL, 8:2) was added NaI (0.30 g, 2 mmol) and trifluoromethanesulphonic acid (0.09 mL, 1 mmol). Triethysilane (0.30 mL, 2 mmol) was slowly added to the mixture and allowed to stir at room temperature for 1 h. The reaction was monitored by GC. The reaction was quenched with 10% $NaHCO_3$ solution (10 mL) on completion and the reaction mass was diluted with DCM (50 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, evaporated and the crude mass was purified by silica gel flash column chromatography (2% ethyl acetate in petroleum ether) to give 4-bromo benzyl iodide **2a** (266 mg, 90%).

1-Bromo-4-(iodomethyl)benzene 2a

White solid; m.p. 71–73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.42 (d, J = 7.9 Hz, 2H), 7.25 (d, J = 7.8, 2H), 4.40 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 131.9, 130.3, 121.6, 4.3. GCMS: 296.

1-Bromo-2-(iodomethyl)benzene 2b

White solid; m.p. 58–60 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.52 (m, 1H), 7.46–7.43 (m, 1H), 7.29–7.23 (m, 1H), 7.15–7.10 (m, 1H), 4.5 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 133.4, 130.5, 129.5, 127.9, 124.0, 5.6; GCMS: 296.

1-Bromo-3-(iodomethyl)benzene 2c

Pale yellow solid; m.p. 50–53 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (t, J = 1.7 Hz, 1H), 7.39–7.36 (m, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 1331.6, 130.9, 130.2, 127.3, 122.4, 3.6; GCMS: 296.

1-Chloro-4-(iodomethyl)benzene 2d

Pale yellow solid; m.p. 62–64 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 2.2 Hz, 2H), 7.28 (d, J = 2.2 Hz, 2H), 4.44 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 133.5, 130.0, 128.9, 4.1; GCMS: 252.

1-Fluoro-2-(iodomethyl)benzene 2e

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.36 (m, 1H), 7.34–7.23 (m, 1H), 7.11–6.99 (m, 2H), 4.45 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 130.7, 129.8, 126.4, 124.4, 115.8, –3.5; GCMS: 236.

2-Chloro-4-fluoro-1-(iodomethyl)benzene 2f

White solid; m.p. 50–52 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 1H), 7.12–7.09 (m, 1H), 6.96–6.92 (m, 1H), 4.49 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 134.5, 132.8, 131.5, 117.4, 114.6, 1.2; GCMS: 270.

1-Bromo-2-fluoro-3-(iodomethyl)benzene 2g

White solid; m.p. 54–56 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.21 (m, 3H), 4.38 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 131.6, 127.8, 125.9, 122.2, 119.5, –4.8; GCMS: 314.

4-Bromo-2-(iodomethyl)-1-methoxybenzene 2h

Off-white solid; m.p. 55–58 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2.4 Hz, 1H), 7.34 (dd, J = 8.72, 2.4 Hz, 1H), 6.72–6.70 (d, J = 8.72 Hz, 1H), 4.40 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 132.6, 132.1, 129.6, 112.7, 112.5, 55.8, –0.7; GCMS: 326.

1-Bromo-3-chloro-2-(iodomethyl)benzene 2i

Off-white solid; m.p. 75–78 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.04 Hz, 1H), 7.33 (d, J = 8.04 Hz, 1H), 7.07 (t, J = 8.04 Hz, 1H), 4.71 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 134.9, 131.9, 129.6, 129.2, 125.1, 125.1, 3.2; GCMS: 331.

1,3-Dichloro-2-(iodomethyl)benzene 2j

White solid; m.p. 63–65 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 7.8 Hz, 2H), 7.15 (t, J = 7.8 Hz, 1H), 4.67 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 134.7, 129.2, 128.5, –0.6; GCMS: 286.

1-(Iodomethyl)-4-isopropylbenzene 2k

Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 6.7 Hz, 2H), 7.16 (d, J = 6.7 Hz, 2H), 4.47 (s, 2H), 2.92–2.85 (m, 1H), 1.24 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 136.5, 128.7, 126.9, 33.8, 23.8, 6.1; GCMS: 260.

2-Iodo-1-(iodomethyl)-4-methoxybenzene 2l

Pale yellow solid; m.p. 58–61 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 2.2 Hz, 1H), 7.25 (dd, J = 8.4, 2.2 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 4.42 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 132.3, 130.5, 128.2, 122.4, 112.1, 56.2, 6.2; GCMS: 373.

Benzyl 4-(iodomethyl)phenyl ether 2m

White solid; m.p. 79–80 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.30 (m, 7H), 6.93–6.89 (m, 2H), 5.06 (s, 2H), 4.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 136.7, 131.6, 130.0, 128.6, 128.0, 127.4, 115.1, 70.0, 6.5; GCMS: 324.

4-(Iodomethyl)benzoic acid 2n

Off-white solid; m.p. 82–85 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.98 (br s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 4.65 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.9, 144.9, 129.9, 129.7, 129.2, 129.1, 5.9; LCMS: 263 (M+1).

Methyl 4-(iodomethyl)benzoate 2o

White solid; m.p. 76–78 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 4.46 (s, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.3, 130.0, 129.5, 128.7, 128.6, 52.1, 3.8; GCMS: 276.

1-[3-(Iodomethyl)phenyl]ethanone 2p

Off-white solid; m.p. 70–72 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 1.5 Hz, 1H), 7.85–82 (dd, J = 7.7, 1.5 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 4.49 (s, 2H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 139.9, 137.5, 133.2, 129.1, 128.2, 127.7, 26.6, 4.0; GCMS: 260.

4-(Iodomethyl)benzonitrile 2q

Yellow solid; m.p. 143–146 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 4.44 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.6, 132.5, 129.3, 118.3, 111.5, 2.7; GCMS: 243.

3-(Iodomethyl)benzonitrile 2r

Pale yellow solid; m.p. 115–117 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.61 (d, J = 7.0 Hz, 1H), 7.54–7.53 (d, J = 7.0 Hz, 1H), 7.44–7.42 (d, J = 7.0 Hz, 1H), 4.42 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 133.0, 132.0, 131.2, 129.6, 118.2, 112.8, 2.5; GCMS: 243.

1-(Iodomethyl)-3-nitrobenzene 2s

Yellow solid; m.p. 84–85 ºC; ^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.25 (t, *J* = 1.9 Hz, 1H), 8.13–8.11 (m, 1H), 7.71 (d, *J* = 7.9, 1.2 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 4.51 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 141.3, 134.6, 129.81, 123.4, 122.6, 2.06; GCMS: 263.

1-(Allyloxy)-2-(iodomethyl)benzene 2t

Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.16 (m, 2H), 6.91–6.81 (m, 2H), 6.18–6.07 (m, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 4.7 Hz, 2H), 4.53 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 133.0, 130.1, 129.4, 127.6, 120.7, 117.2, 112.1, 68.6, 1.2; GCMS: 274.

1-(Allyloxy)-4-(iodomethyl)benzene 2u

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 6.87–6.83 (m, 2H), 6.08–6.05 (m, 1H), 5.44 (d, *J* = 16.8 Hz, 1H), 5.29 (d, *J* = 10.0 Hz, 1H), 4.65 (d, *J* = 4.8 Hz, 2H), 4.54 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 135.6, 133.4, 129.9, 117.7, 115.0, 68.7, 5.5; GCMS: 274.

[(1-*E*)-3-Iodopro-1-en-1-yl]benzene 2v

Pale yellow solid; m.p. 58–60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.23 (m, 5H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.50–6.40 (m, 1H), 4.14 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8, 133.0, 128.5, 128.1, 126.8, 126.5, 6.7; GCMS: 244.

1-Ethynyl-4-(iodomethyl)benzene 2w

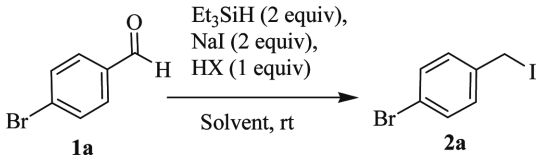
Pale yellow solid; m.p. 52–53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.44 (s, 2H), 3.10 (s, *J* = 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 132.4, 128.6, 121.6, 83.1, 77.8, 4.5; GCMS: 242.

1-(Iodomethyl)-4-(phenylethynyl)benzene 2x

Pale yellow solid; m.p. 54–56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.62 (m, 2H), 7.53–7.50 (m, 1H), 7.46–7.39 (m, 5H), 7.37–7.25 (m, 1H), 4.71 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 132.5, 131.5, 128.9, 128.7, 128.5, 128.4, 128.1, 127.9, 125.6, 123.1, 122.7, 95.8, 86.6, 4.4; GCMS: 318.

RESULTS AND DISCUSSION

To execute this task, *p*-bromobenzaldehyde **1a**, a model substrate shown in *Scheme* 1, was stirred with Et_3SiH, TfOH and NaI as an iodide source in acetonitrile at room temperature for 2 h furnished **2a** in 75% yield (*Table* 1). To further optimize conditions, the reaction was conducted



1a **2a**

***Scheme* 1.** Reductive iodination of *p*-bromobenzaldehyde.

***Table* 1.** Optimization of reductive iodination condition with various solvents and protic acids[a]

Entry	Acids	Solvents	Time (h)	Yield[b] (%)
1	TfOH	CH_3CN	12	75
2	TfOH	DME	12	35
3	TfOH	Toluene	12	15
4	TfOH	THF	12	trace
5	TfOH	DMF	12	–
6	TfOH	DCM	12	trace
7	CH_3COOH	CH_3CN	12	–
8	TFA	CH_3CN	12	–
9	$MeSO_3H$	CH_3CN	12	trace
10	TfOH	CH_3CN/DME	1	90

[a]Reactions were performed on *p*-bromobenzaldehyde (1 mmol) in CH_3CN (5 mL) with 2 equiv. of triethylsilane (Et_3SiH), 1 2 equiv. of acid, 2 equiv. of NaI. [b]Isolated yield. DME: 1,2-dimethoxyethane.

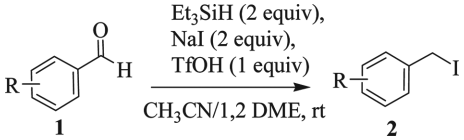
by changing the solvents, Brønsted acids and reaction time.

Solvents such as DME and toluene did not improve the yield and formation of the desired product was not observed when the reaction was carried out in THF, DMF and DCM (entry 2–6). Similar results were obtained when the reaction was conducted in the presence of various protic acids. Surprisingly, using the mixture of acetonitrile/DME (8:2) with TfOH resulted in complete consumption of **1a** in 1 h and delivered **2a** in high yield (90%) (*Table* 1).[9a,b] Additionally, nBu$_4$NI and nMe$_4$NI were used as iodide source instead of sodium iodide under the optimized condition (entry 10) showed complete decomposition.

In order to explore the application of this protocol, we employed the optimized conditions on benzaldehydes bearing various functional groups. Bromo, chloro, fluoro substituted benzaldehydes **1b**–**1j** underwent smooth reductive iodination to deliver the corresponding benzyl iodides **2b**–**2j** in high yield (*Table* 2). Similarly, alkyl and alkoxy substituted benzaldehydes gave the desired products **2k**–**2m**. Carbonyl derivatives such as acid and ester group bearing benzaldehydes led to the corresponding benzyl iodides **2n**–**2o** in high yield. The desired benzyl iodide **2p** was obtained in high yield without affecting the keto functionality. Nitro and cyano substituted benzaldehydes also delivered the desired products **2q**–**2s** as shown in the *Table* 2.

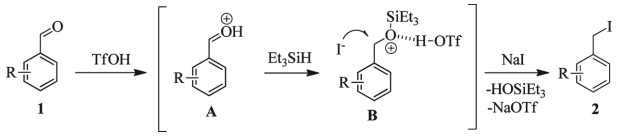
To further demonstrate the efficiency of this protocol, allyl substituted benzaldehydes were converted into corresponding the benzyl iodide derivatives **2t**–**2u**. Cinnamaldehyde led to the iodo derivative **2v** wherein the double bond is preserved. Triple bonds also remained unaffected when terminal and internal alkyne substituted benzaldehydes were subjected to the reductive iodination to afford **2w**–**2x** (*Table* 2). However, aliphatic aldehydes fail to

***Table* 2.** Synthesis of various benzyl iodides through a reductive iodination



Entry	Aldehyde	Product	Time (min)	Yield[a] (%)	Mp (°C)/(lit.)
1	4-BrC_6H_4 CHO	**2a**	60	90	71–73
2	2-BrC_6H_4CHO	**2b**	30	90	58–60
3	3-BrC_6H_4CHO	**2c**	45	89	50–55
4	4-ClC_6H_4CHO	**2d**	60	87	62–64
5	2-FC_6H_4CHO	**2e**	45	88	
6	2-Cl,4-FC_6H_3CHO	**2f**	45	85	50–52
7	3-Br,2-FC_6H_3CHO	**2g**	60	84	54–56
8	5-Br,2-$OMeC_6H_3$CHO	**2h**	50	83	55–58
9	2-Br,6-ClC_6H_3CHO	**2i**	60	86	75–78
10	2-Cl,6-ClC_6H_3CHO	**2j**	60	90	63–65
11	4-$iPrC_6H_4$CHO	**2k**	45	87	
12	2-I,4-$OMeC_6H_3$CHO	**2l**	60	78	58–61
13	4-$OBnC_6H_4$CHO	**2m**	35	75	79–80
14	4-$COOHC_6H_4$CHO	**2n**	30	85	82–85
15	4-$COOCH_3C_6H_4$CHO	**2o**	35	87	76–78
16	3-$COCH_3C_6H_4$CHO	**2p**	45	88	70–72
17	4-CNC_6H_4CHO	**2q**	50	73	143–146
18	3-CNC_6H_4CHO	**2r**	38	75	115–117
19	3-$O_2NC_6H_4$CHO	**2s**	45	76	84–85
20	2-AllyloxyC_6H_4CHO	**2t**	50	78	
21	4-AllyloxyC_6H_4CHO	**2u**	38	76	58–60
22	Cinnamaldehyde	**2v**	50	82	52–53
23	4-Ethynylbenzaldehyde	**2w**	30	72	54–56
24	4-(Phenylethynyl)benzaldehyde	**2x**	40	81	152–153

[a]Isolated yields.



***Scheme* 2.** Tentative mechanism for reductive iodination.

undergo reductive iodination.

A tentative mechanism has been shown in *Scheme* 2 for the reductive iodination. At first, the aldehyde **1** gets protonated to form a protonated aldehyde **A** which undergoes reduction under Et_3SiH to generate **B**. Nucleophilic displacement on **B** with iodide gives benzyl iodide **2**.

CONCLUSION

In conclusion, we have developed a simple and efficient protocol for the preparation of benzyl iodides from aryl aldehydes in a single step through a reductive iodination protocol. This transformation was performed under ambient condition using a combination Et_3SiH, CF_3SO_3H and NaI. Also, it exhibits broad functional group tolerance.

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9. (a) In our hands, lower conversion was observed when TfOH was used in catalytic amount (25 mol %) whereas complete conversion was seen with 1 equiv. of TfOH under the reaction condition; (b) Similarly, no product formation was not observed under Lewis acid condition.