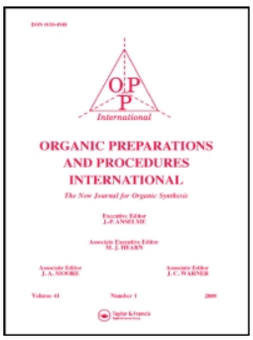

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Identification of the Iodination and Bromination Products of 3-Hydroxybenzaldehyde: Preparation of 5-Hydroxy-2-iodobenzaldehyde

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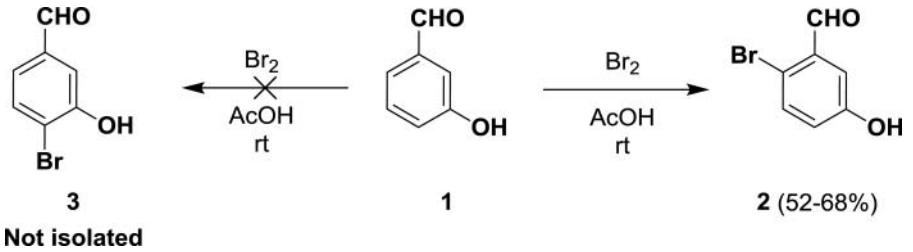
The monohalogenation products of 3-hydroxybenzaldehyde (**1**) are useful synthons for the preparation of more complex molecules.[1–4] For example, the introduction of a halogen allows the use of a Suzuki-type coupling for the preparation of substituted biphenyls.[5] However, monohalogenated derivatives of **1** have been the subject of a certain amount of controversy in the past, with several papers incorrectly assigning the chemical structures of the regioisomers isolated. For example, while Pandya et al. reported a method for the direct bromination of **1** to afford 4-bromo-3-hydroxybenzaldehyde (**3**) under acidic conditions in 1952,[6] Barfknecht et al. later determined that the product obtained under these conditions was actually 2-bromo-5-hydroxybenzaldehyde **2** (*Scheme 1*).[7]



Scheme 1 Results of the monobromination of **1** under acidic conditions.

This confusing situation has given rise to a certain amount of debate in the literature.[8,9] Morin *et al.* addressed this problem by preparing[10] and characterizing compounds **2** and **3** from **1** *via* different synthetic routes, but unfortunately mis-assigned the NMR data for those two compounds in the additional information section. [11] Fortunately, the structure of **2** had been accurately established previously by Paixao's group with the aid

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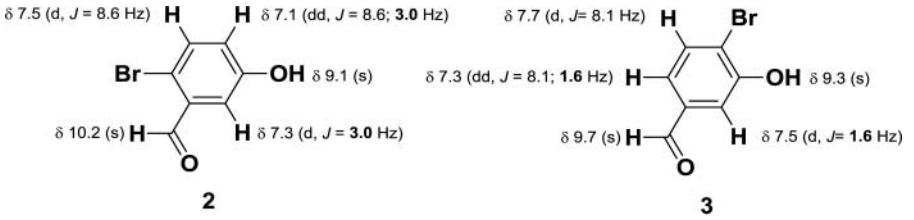
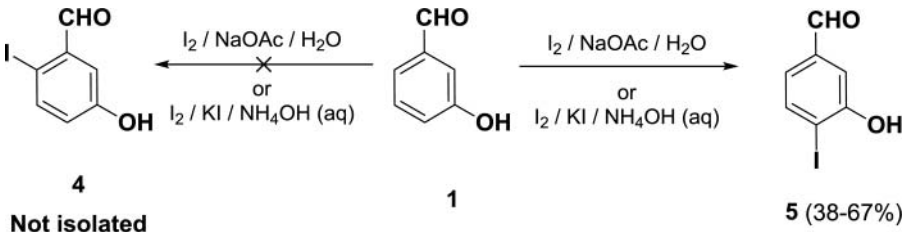


Figure 1 Chemical shifts (in δ) and coupling constants of the monobrominated regioisomers **2** and **3** in acetone-d_6.

of NMR and X-ray diffraction techniques, which clarified the situation and confirmed that the major bromination product of 3-hydroxybenzaldehyde with bromine in acetic acid is indeed 2-bromo-5-hydroxybenzaldehyde **2**.[12]

Figure 1 shows the chemical shifts and coupling constants in the ^{1}H NMR spectra of compounds **2** and **3**.[10] As will be seen below, these data are of particular interest because it is possible to correlate the structure of the monohalogenation product with the *meta* coupling constant, which is significantly different for compounds **2** and **3**.

Unfortunately, this confusion in the literature is not limited to the monobromination products of **1**. Thus, in 1937, Hodgson and Smith described a monoiodination of **1** in basic medium in which the major product was claimed to be 5-hydroxy-2-iodobenzaldehyde (**4**),[13] a premise supported by Letcher *et al.* in 1977.[15] It was not until 1987 that Sternhell *et al.* correctly identified the structure of the major product obtained by Hodgson to be 3-hydroxy-4-iodobenzaldehyde (**5**, Sc*heme 2*).[14] In 1952, Pandya *et al.* reported a different method for the preparation of 5-hydroxy-2-iodobenzaldehyde (**4**) by direct iodination of **1** in aqueous ammonia.[6] As was the case with Hodgson's route, it displayed little regioselectivity and afforded a mixture of monoiodinated products **4** and **5** together with the corresponding diiodinated product (*Scheme 2*): The major product from Pandya's synthesis[6] was isolated after precipitation in acidic medium followed by crystallization of the crude product. Our attempts to prepare compound **4** with this method raised doubts about the structure assigned by Pandya to the major reaction product, especially after comparison of its NMR spectra with its brominated analog, the structure of which had already been unambiguously assigned by Paixao *et al.*[12] As will be shown below, the *meta* coupling constant in the major product of Pandya's synthesis is more similar to that of monobrominated compound **3**, which displays the halogen atom *ortho* to the hydroxy group, than to that of compound **2**, which we had prepared following Morin's procedure.[10] Moreover, comparison of the HMBC spectrum of the major reaction product with that described[10] for **5** clearly showed that its structure is that of 3-hydroxy-4-iodobenzaldehyde (**5**) rather than that of 5-hydroxy-2-iodobenzaldehyde (**4**) as Pandya had reported



Scheme 2 Direct iodination of 1 in basic medium.[16].

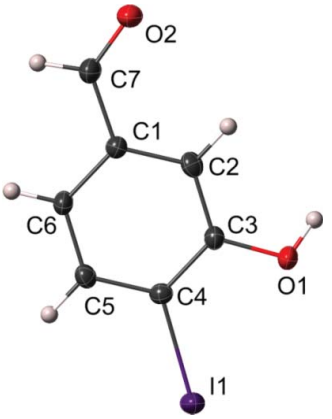
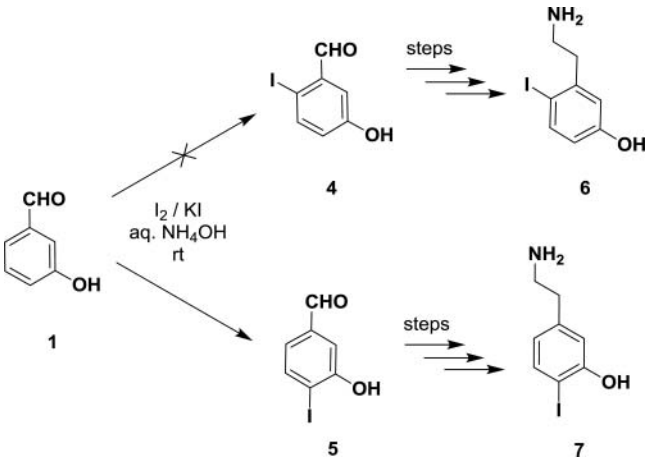


Figure 2 Ellipsoid plot of **5** (50% probability level), showing the labelling scheme.

(*Scheme 2*) since it shows clear correlations between the OH hydrogen and C2 (d), C3 (s), and C4 (s). Finally, the structure of **5** was unambiguously confirmed by means of X-ray diffraction techniques. Thus, single crystals of **5** suitable for X-ray diffraction experiments were prepared by slow evaporation of a diethyl ether solution. The X-ray structure of (**5**) unambiguously confirmed the proposed 3-hydroxy-4-iodobenzaldehyde structure for this compound (see *Figure 2*).

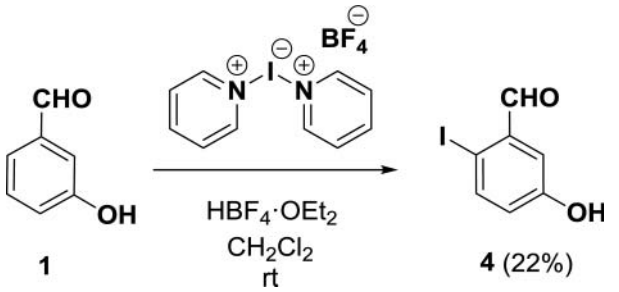
Interestingly, Rocha Gonsalves *et al.* recently reproduced Pandya's procedure and assigned structure **5** to the major monoiodination product;[17] however, the authors provided no reason or explanation for this specific change in structural assignment.

Pandya's monoiodination method was also used by Counsell *et al.* for the preparation of iodinated tyramines.[18] Unfortunately, Counsell included no details or spectroscopic data with regard to the iodination product of **1**, asserting that it was the minor regioisomer **4**. It is, however, much more likely that the starting compound for their synthesis is actually its isomer **5**, which means that the structure of the resulting iodinated tyramine is not **6** as reported by Counsell, but most likely **7** (*Scheme 3*).



Scheme 3 Counsell's preparation of an iodinated tyramine.

Once we had correctly identified the monoiodinated derivative **5**, our next goal was to devise a synthesis of its regioisomer **4**; though a commercially available reagent, to the best of our knowledge, its preparation has not been reported to date. After several unsuccessful attempts, the direct monoiodination of **1** using the commercially available reagent *bis*(pyridyl)iodonium(I) tetrafluoroborate gave compound **4**, albeit in only low yield (22%), (*Scheme 4*).[19] Although this reaction, which takes place in an acidic medium, gives rise to a complex mixture, direct crystallization of the complex crude product affords a pure compound that we were able to identify as the desired regioisomer **4**. Although we could not obtain a suitable monocrystal for X-ray determination, its ^{1}H NMR spectrum shows a typical 1,2,4 pattern for the three aromatic H atoms (*Fig. 3*). In contrast to compound **5**, which displays a *meta* coupling constant of 1.8 Hz (similar to that of 1.6 Hz for its brominated analog **3**), compound **4** shows a *meta* coupling constant of 3.1 Hz [similar (3.0 Hz) to that of its brominated analog **2**]. Thus, by analogy with compounds **2** and **3**, we can state that *bis*(pyridyl)iodonium(I) tetrafluoroborate as iodinating reagent allows the preparation of **4**. The HMBC spectrum of the major reaction product agreed with its structure being 5-hydroxy-2-iodobenzaldehyde (**4**). Thus, the OH hydrogen correlates now with C4 (d), C5 (s), and C6 (d), which confirms that in compound **4** the OH group is between two CH groups.



Scheme 4 Preparation of **4** from **1**.

When the coupling constants of compounds **2**-**5** are compared, it is possible to draw some useful conclusions about the effect of substitution pattern on the iodination and bromination products of compound **1**. In fact, those patterns can be used to determine which compound is formed in the direct monohalogenation of **1**. Coupling constants in ^{1}H NMR spectra are quite independent both of the solvent used and of the measurement temperature (as long as these do not affect conformational equilibria), and therefore constitute a

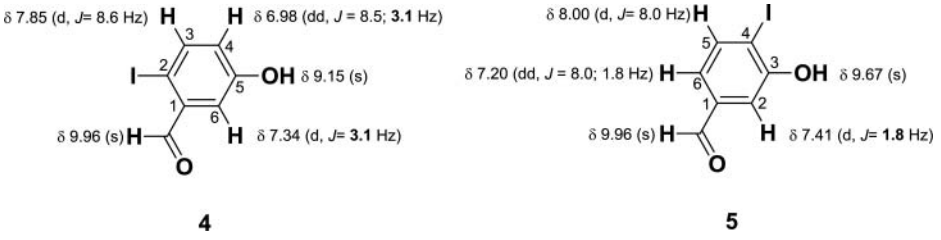
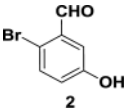
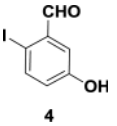
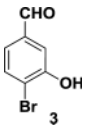
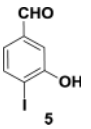


Figure 3 Chemical shifts (in δ) and coupling constants of the monoiodinated regioisomers **4** and **5** in acetone-d_6.

Table 1
Comparison of *ortho* and *meta* Coupling Constants of Compounds **2**-**5**

Compound	(in CD_3COCD_3)	Compound	(in CD_3COCD_3)	(in $CDCl_3$)
 **2**	$J_{ortho} = 8.6$ Hz $J_{meta} = 3.0$ Hz	 **4**	$J_{ortho} = 8.6$ Hz $J_{meta} = 3.1$ Hz	$J_{ortho} = 8.4$ Hz $J_{meta} = 3.0$ Hz
 **3**	$J_{ortho} = 8.1$ Hz $J_{meta} = 1.6$ Hz	 **5**	$J_{ortho} = 8.0$ Hz $J_{meta} = 1.8$ Hz	$J_{ortho} = 8.1$ Hz $J_{meta} = 1.8$ Hz

rapid method to check for structural assignment errors in monohalogenated derivatives of **1**. It is evident from *Table 1* that when the bromine or iodine atom is introduced in the *ortho* position to the hydroxy group (as in compounds **3** and **5**), the *meta* coupling constant is significantly lower (1.6–1.8 Hz) than when it is introduced in the *para* position relative to the same group (3.0–3.1 Hz).

Using this correlation to examine the spectroscopic data of previously reported iodination products of **1**, it should be easy to detect further possible errors in structural assignments. Aside from Letcher's paper,[15] which has already been discussed above as having mistakenly described the monoiodination product of **1** as 5-hydroxy-2-iodo-benzaldehyde (**4**) - when it is in fact its isomer **5** - a paper by Vibhute *et al.*[20] contains yet another error, namely an erroneous m.p. for 3-hydroxy-4-iodobenzaldehyde **5**.[21]Two additional publications describing the preparation of 3-hydroxy-4-iodobenzaldehyde (**5**) are correct in their structural assignment for the product in both cases.[22,23]

In summary, we hope that the present paper will clarify the confusion about the correct structure of the monoiodinated and monobrominated derivatives of 3-hydroxybenzaldehyde **1**: Pandya's iodination of **1** affords its monoiodinated derivative **5** as the major product rather than its regioisomer **4**, as originally reported. The magnitude of the *meta* coupling constant in the ^{1}H NMR spectra can be conveniently used to determine quickly which isomer has been obtained in each case. The direct monoiodination method for **1** with *bis*(pyridyl)iodonium(I) tetrafluoroborate to provide **4** as the major product has been described for the first time. This is significant because all the monoiodination methods found in the literature describe only the preparation of **5** from **1**. Even though our reaction gives a low yield, the desired regioisomer **4** can be conveniently obtained pure from the crude reaction mixture by means of a simple crystallization.

Experimental Section

Materials and Methods

All starting materials, reagents, and solvents were obtained from commercial sources (Aldrich and Merck) and used without further purification. Thin layer chromatography

(TLC) was performed on Merck GF/UV 254 plates, and visualized with UV light at 254 nm. Melting points were measured using a Buchi M-560 melting-point and are uncorrected. All of the NMR spectra were recorded on a Bruker Avance 300 DRX (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR), with chemical shifts expressed as values relative to tetramethylsilane as the internal standard and coupling constants (J values) given in Hertz (Hz). High resolution mass spectra (HRMS) spectra were recorded on a TRIPLETOF^{T}5600 (ABSciex) with Electrospray Ionization in the positive ion mode.

5-Hydroxy-2-iodobenzaldehyde (4)

To a solution of 1.0 g (8.18 mmol) of 3-hydroxybenzaldehyde in 100 mL of dichloromethane, was slowly added 1.078 g (12.28 mmol) of $HBF_4{\cdot}OEt_2$ at r.t., followed by the addition of 3.045 g (8.18 mmol) of IPy_2BF_4 *bis*(pyridyl)iodonium(I) tetrafluoroborate. The solution was stirred for 5 min at r.t., after which a solution of 15 mL of 1M HCl were added in 15 mL of water. The aqueous layer was extracted with dichloromethane (3 × 10 mL) and the combined organic layers were washed with 10 mL water and 25 mL 5% sodium thiosulfate aqueous solution and dried over Na_2SO_4. Removal of the volatiles under reduced pressure afforded a brownish solid, which was recrystallized from chloroform to afford 443 mg (22%) of 5-hydroxy-2-iodobenzaldehyde 4 as a brownish solid, mp. 130–132°C, *lit.* mp. 125–126°C.[24] ^{1}H NMR (300 MHz, CD_3COCD_3): δ 9.96 (s, 1H), 9.15 (s, 1H), 7.85 (d, $J = 8.6$ Hz, 1H), 7.34 (d, $J = 3.1$ Hz, 1H), 6.98 (dd, $J_1 = 8.5$ Hz, $J_2 = 3.1$ Hz, 1H); ^{1}H RMN (300 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.45 (d, $J = 3.0$ Hz, 1H), 6.91 (dd, $J_1 = 8.4$ Hz, $J_2 = 3.0$ Hz, 1H), 6.18 (br s, 1H); ^{13}C RMN (75 MHz, CD_3COCD_3): δ 196.6 (CHO), 160.1 (C-5), 143.3 (C-3), 137.9 (C-1), 125.4 (C-4), 118.1 (C-6), 88.5 (C-2); ^{13}C RMN (75 MHz, $CDCl_3$) δ ppm: 196.3 (CHO), 156.7 (C-5), 141.4 (C-3), 135.7 (C-1), 123.9 (C-4), 116.5 (C-6), 89.4 (C-2); HRMS (EI) m/z: Calcd for $C_7H_5IO_2$: 247.9334. Found: 247.9292.

3-Hydroxy-4-iodobenzaldehyde (5)

3-Hydroxybenzaldehyde (1.60 g, 13.18 mmol) was dissolved in 15 mL of 33% aqueous NH_4OH in a 100 mL round-bottomed flask. Separately, iodine (3.72 g, 14.65 mmol) was added to 25 mL of 30% (w/v) solution of KI in water. The latter solution was added dropwise to the 3-hydroxybenzaldehyde solution, after which the reaction was stirred at rt for 2h. The reaction mixture was cooled then with an ice bath and made acid with conc. HCl, which caused the appearance of a yellow gum. The gum was taken up in Et_2O, and the remaining aqueous solution was extracted with more Et_2O (3 × 10 mL). The organic layers were pooled together, washed with 10 mL of an aqueous saturated solution of $Na_2S_2O_3$, and dried over anh. Na_2SO_4. After filtration and solvent removal under reduced pressure, an orange-colored solid is obtained, which was crystallized from Et_2O to afford 927 mg of 3-hydroxy-4-iodobenzaldehyde **5** as a yellowish solid. Yield: 28%. M.p.: 128–130°C, *lit.* mp. 128–129 °C.[25] ^{1}H RMN (300 MHz, CD_3COCD_3): δ 9.94 (s, 1H), 9.67 (s, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.41 (d, $J = 1.8$ Hz, 1H), 7.20 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.8$ Hz, 1H); ^{1}H RMN (300 MHz, $CDCl_3$) δ ppm: 9.92 (s, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.44 (d, $J = 1.8$ Hz, 1H), 7.18 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.8$ Hz, 1H), 5.93 (br s, 1H); ^{13}C RMN (75 MHz, CD_3COCD_3): δ 193.2 (CHO), 159.2 (C-3), 142.1 (C-5), 140.2 (C-1), 124.5 (C-6), 115.3 (C-2), 94.0 (C-4); ^{13}C RMN (75 MHz, $CDCl_3$): δ 191.3 (CHO), 155.8 (C-3), 139.3 (C-5), 138.3 (C-1), 123.0 (C-6), 114.8 (C-2), 93.9 (C-4); HRMS (EI) m/z: Calcd for $C_7H_5IO_2$: 247.9334. Found: 247.9358.

Crystal Data for Compound 5

$C_7H_5IO_2$, $M = 248.01$, monoclinic, $a = 4.493(3)$, $b = 6.826(3)$, $c = 12.031(3)$ Å, $\beta = 92.01(3)°$, $V = 368.8(3)$ Å^3, space group $P2_1$, $Z = 2$, $T = 150(2)$ K, $\lambda = 0.71073$ Å, Dcalcd $= 2.234$ gcm^{-3}, $\mu = 4.273$ cm^{-1}, 3343 reflections measured, 1925 unique ($R_{int} = 0.0303$), crystal structure solved by direct methods with all non hydrogen atoms refined anisotropically on F^2 using the programs SHELXS and SHELXL-2016,[26] hydroxyl hydrogen atom was included as *rigid* others using a *riding* model, R (Fo, $I > 2\sigma(I)) = 0.0235$ Rw (Fo^2, all data) $= 0.0559$. Supporting Information Available: CCDC-1514944 contain the supplementary crystallographic data for compound **5** (www.ccdc.cam.ac.uk/data_request/cif).

2-Bromo-5-hydroxybenzaldehyde (2)[10]

To a stirred solution of 1.5 g (12.3 mmol) of 3-hydroxybenzaldehyde in 10 mL of glacial acetic acid at 22°C was added 2.35 g (14.7 mmol) of bromine so as to keep the temperature at or below 22°. After stirring overnight at r.t., the volatiles were removed under reduced pressure. The residue was washed with hexane (3 × 15 mL) and then taken up in warm chloroform. After cooling, a total of 1.35 g (55%) of 2-bromo-5-hydroxybenzaldehyde 2 was obtained in two crops. Mp: 132–134°C, *lit.* mp 134 °C.[27] ^{1}H RMN (300 MHz, CD_3COCD_3) δ ppm: 10.24 (s, 1H), 9.05 (s, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.34 (d, $J = 3.1$ Hz, 1H), 7.10 (dd, $J_1 = 8.7$ Hz, $J_2 = 3.1$ Hz, 1H); ^{13}C RMN (75 MHz, CD_3COCD_3) δ ppm: 192.8 (CHO), 159.3 (C-5), 136.7 (C-6), 136.2 (C-1), 125.1 (C-4), 117.3 (C-3), 117.2 (C-2); HRMS (EI) m/z: Calcd for $C_7H_5BrO_2$: 199.9472. Found: 199.9463.

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16. The broad yield interval for the preparation of **5** shown in this scheme (38–67%) reflects published yields. In our own experience with this reaction, however, the yield is more in agreement with a lower range of *ca*. 30%.

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21. We have repeated the procedure described in reference 20 and determined that the product is indeed isomer **5** as described by the authors. However, they describe the m.p. of **5** as 182°C, when it should be 128–130°C.

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24. Even though compound **4** is commercially available, there are no experimental procedures described in the literature for its preparation and the only m.p. data come from commercial suppliers. For instance, Cambridge Chemicals mentions an m.p. of 125–126°C for a 97% purity (catalog number B219130, see http://www.cambridgechem.com/5-hydroxy-2-iodobenzalde hyde). Another supplier, Ark Pharm, Inc. mentions an m.p. of 125°C for a 97% purity (catalog number AK-81430, see http://www.arkpharminc.com/product/detail/AK-81430.html). As a further example, Astatech mentions an m.p. of 125–126°C for a 95% purity (catalog number 62528, see http://www.astatechinc.com/CPSResult.php?CRNO=6982).

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