Combination of $NH_2OH·HCl$ and $NaIO_4$: a new and mild reagent for the synthesis of vicinal diiodo carbonyl compounds

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Abstract

The synthesis of vicinal diiodo carbonyl compounds from α,β-unsaturated carbonyl compounds has been carried out for the first time using the combination of $NH_2OH·HCl$ and $NaIO_4$ under mild reaction conditions at room temperature. The present methodology is also applicable for the synthesis of vicinal diiodo derivatives of nitrostyrene. The remarkable advantages of the present protocol are room temperature reaction, easy operation, good yields, fast reaction, transition metal-free and neutral reaction conditions. The present methodology is applicable to gram scale synthesis.

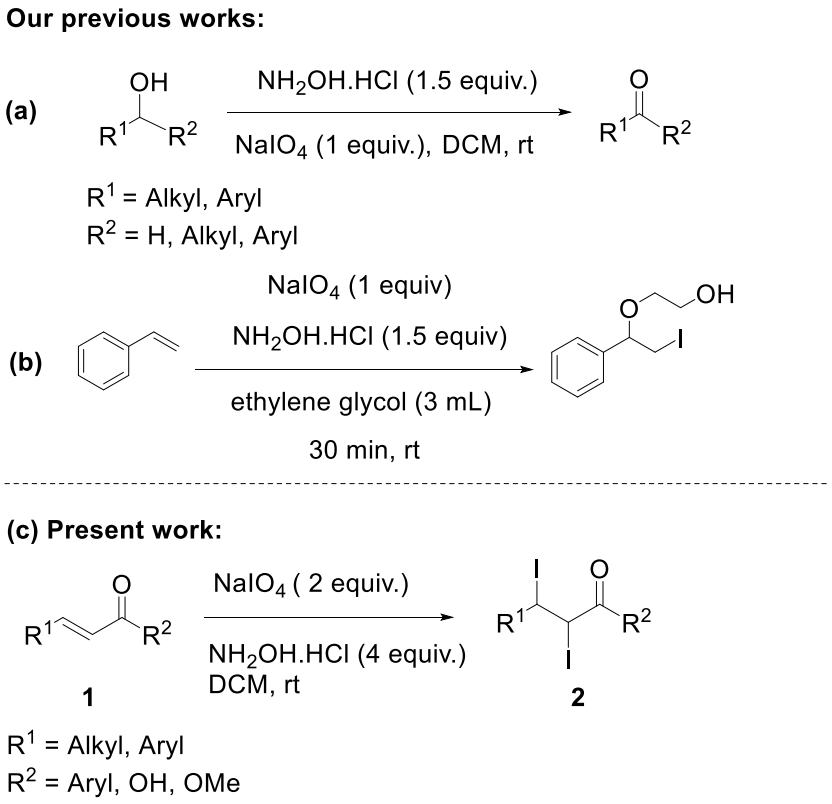
Keywords: Carbonyl compounds, hydroxylamine hydrochloride, sodium periodate, vicinal diiodination

Introduction

The search for a new reagent and its systematic investigation is very much meaningful to synthetic organic chemists. Organic haloalkanes are extensively used for carbon-heteroatom bond forming reactions[1] as well as the carbon-metal atom bond formation such as Grignard's reagent,[2-5] carbenoids[6-7] etc. Specifically, carbenoids are preferentially prepared from iodoalkanes since they are more reactive than other haloalkanes.[8] The preparation of the iodoalkanes is more difficult due to the high C–I bond reactivity[9-14] and diiodoalkanes are even more difficult. Although some reported methods have been achieved to prepare *gem* diiodoalkanes,[15-18] to the best of our knowledge there is no general method to prepare vicinal diiodoalkane compounds. In a strained system like norbornene it is feasible due to relief of strain,[19] but if 1,2-diiodoalkane forms in the reaction medium it reversibly loses I_2 to reform the alkene.[20] So the preparation of vicinal diiodo

compounds is a matter of interest. We are actively engaged in developing new reagents and methodologies in organic synthesis.[21-23]

Very recently, we have reported the combination of $NaIO_4$ and $NH_2OH{\cdot}HCl$ as a good, selective and mild oxidizing agent for the oxidation of alcohols to the corresponding carbonyl compounds at room temperature[24] (Scheme 1, a) and preparation of β-iodo-β′-hydroxy ethers, β-iodo ethers, β-iodohydrin, and β-iodoacetoxy compounds using different reaction media (nucleophiles) (Scheme 1, b).[25] For further application of this reagent system herein, we report the synthesis of α,β-diiodo carbonyl compounds (**2**) from α,β-unsaturated carbonyl compounds (**1**) using (Scheme 1, c).



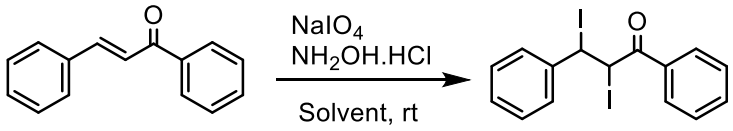
Scheme 1. Oxidation, regioselective 1,2-difunctionalization and vicinal diiodination of conjugated double bonds.

Results and Discussion

For optimization of the reagents combination we chose different ratios of $NaIO_4$ and $NH_2OH{\cdot}HCl$ as shown in Table 1 using simple chalcone (**1a**) as model substrate. First of all we used 1:1 proportion of $NaIO_4$ and $NH_2OH{\cdot}HCl$ and very lower amount (20%) of desired product (**2a**) was observed (entry 1, Table 1). By increasing the proportion of $NH_2OH{\cdot}HCl$ from 1 to 1.5 the yield

of the desired product (**2a**) was increased to 40% (entries 2-4, Table 1). The maximum amount of yield was obtained by using 2:4 ratios of $NaIO_4$ and $NH_2OH{\cdot}HCl$ respectively (entry 5, Table 1). Further increasing the amount of both the reagents in different ratios the yield of the diiodo product did not improve significantly (entries 6-7, Table 1). We have also examined the role of solvent for this reaction and found that solvent plays a vital role in the reaction. Only dichloromethane (DCM) and 1,2-dichloroethane (1,2-DCE) act as a good solvent for these particular reactions. In presence of other solvents, such as acetonitrile, THF, 1,4-dioxane, toluene and hexane the reaction did not work well (yields are less than 15%, entries 8-10, 12, 13, Table 1). In addition, no desired diiodo product has been detected by using methanol as solvent (entry 14, Table 1). 1,2-Dichloroethane as solvent afforded a good yield (75%, Table 1, entry 11) but not as good as dichloromethane. Finally, optimized reaction conditions were obtained using 2 equiv. of $NaIO_4$ and 4 equiv. of $NH_2OH{\cdot}HCl$ with respect to the 1 equiv. of α,β-unsaturated carbonyl compounds (**1**) in DCM (2 mL) at room temperature (Table 1, entry 5).

Table 1. Optimization of the reaction conditions [a]



1a **2a**

Entry	C=C:$NaIO_4$:$NH_2OH{\cdot}HCl$	Solvent (2 mL)	Yield[b] (%)
1	1 : 1 : 1	DCM	20
2	1 : 1 : 1.5	DCM	30
3	1 : 1 : 2	DCM	34
4	1 : 2 : 3	DCM	40
5	1 : 2 : 4	DCM	84
6	1 : 2 : 5	DCM	84
7	1 : 2.5 : 5	DCM	82
8	1 : 2 : 4	MeCN	14
9	1 : 2 : 4	THF	12
10	1 : 2 : 4	1,4-Dioxane	<10
11	1 : 2 : 4	1,2-DCE	75
12	1 : 2 : 4	Toluene	NR
13	1 : 2 : 4	Hexane	NR
14	1 : 2 : 4	MeOH	NR

[a] Reaction conditions: 1 mmol of chalcone (**1a**) with various proportions of $NaIO_4$ and $NH_2OH{\cdot}HCl$ in solvent (2 mL). [b] Isolated yields. NR = No reaction.

With optimized reaction conditions in hand, the scope and limitations of this reaction were investigated. Different α,β-unsaturated carbonyl compounds were subjected to give the

corresponding diiodo compounds. The reaction proceeded well with chalcones (**1a**, **1b**, **1c**, **1d**) and unsaturated acids (**1d**, **1e**), affording the vicinal diiodo derivatives (**2a**-**2e**) with satisfactory yields. The α,β-unsaturated ester (**1f**) underwent the reaction without any hydrolyzed product. Functional groups like –Cl, -NO_2 in chalcone were also unaffected under the present reaction conditions to afford the desired products (**2b**, **2c**). Chalcone containing electron donating –OMe group on the aromatic ring have shown also good efficiency (**2d**). When dibenzylidene acetone (**1h**) was subjected to these conditions using 4 equiv. of $NaIO_4$, 8 equiv. of $NH_2OH{\cdot}HCl$, the expected tetraiodo product (**2h**) was obtained with high yield (entry 8, Table 2). The results are summarized in Table 2.

Table 2. Diiodination of α,β-unsaturated carbonyl compounds [a]

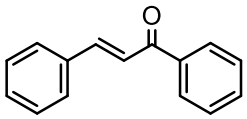
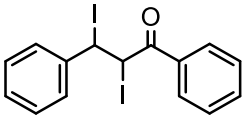
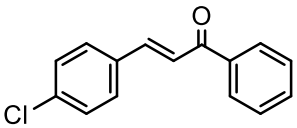
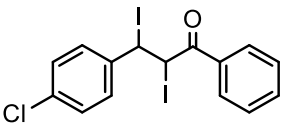
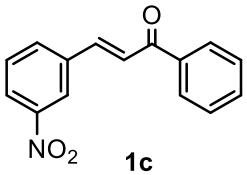
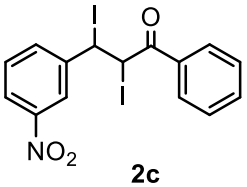
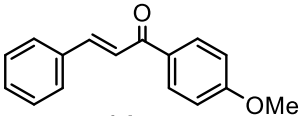
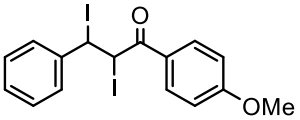
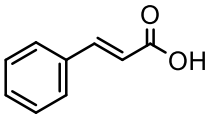
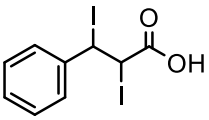
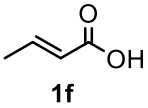
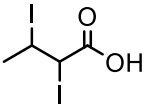
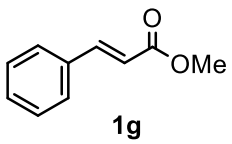
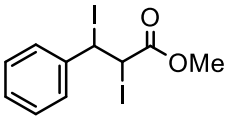
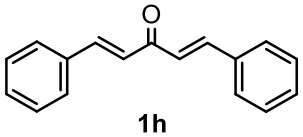
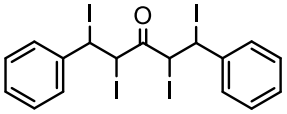
Entry	Substrates	Products	Yields [b]
1	 **1a**	 **2a**	84%
2	 **1b**	 **2b**	81%
3	 **1c**	 **2c**	82%
4	 **1d**	 **2d**	80%
5	 **1e**	 **2e**	83%
6	 **1f**	 **2f**	81%

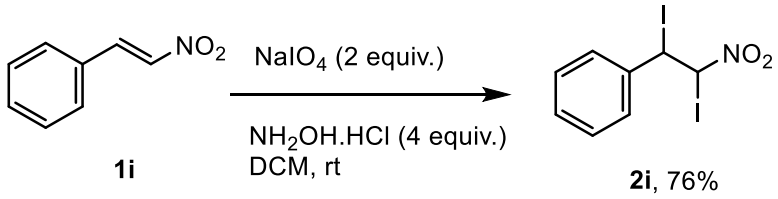
Table 2 (continued)

Entry	Substrates	Products	Yields b

7	 1g	 2g	84%
8[c]	 1h	 2h	82%

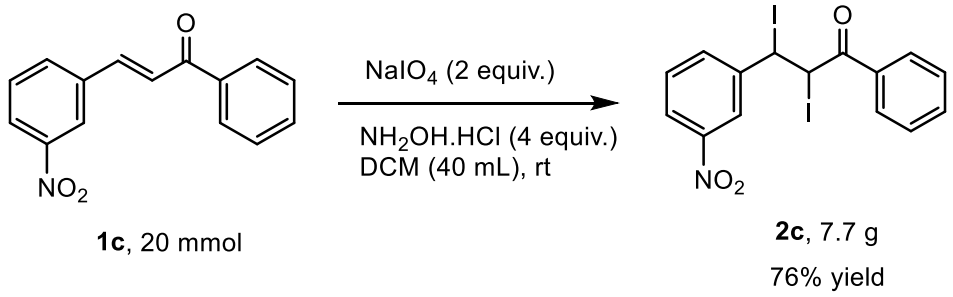
[a] Reaction conditions: 1 mmol of olefin (**1**), 2 equiv. of $NaIO_4$, 4 equiv. of $NH_2OH{\cdot}HCl$ in DCM (2 mL). [b] Isolated yields. [c] 4 Equiv. of $NaIO_4$ and 8 equiv. of $NH_2OH{\cdot}HCl$ were used.

Another important observation of this protocol is the reaction of nitrostyrene (**1i**) under the same reaction conditions to give 1,2-diiodo nitro derivative (**2i**) in 76% yield (Scheme 2). This compound is synthetically very useful as it contains a nitro group and two excellent leaving groups which can readily be replaced by a heteroatom and can be applied in C-C coupling reactions.



Scheme 2. Diiodination of nitrostyrene.

The applicability of this methodology is demonstrated for the synthesis on gram scale. The treatment of 20 mmol of (*E*)-3-(3-nitrophenyl)-1-phenylprop-2-en-1-one (**1c**) with 2 equiv. of $NaIO_4$, 4 equiv. of $NH_2OH{\cdot}HCl$ at room temperature in 40 mL of DCM afforded the corresponding diiodo product (**2c**) in 76% yield (Scheme 3).



Scheme 3. Application on gram-scale synthesis.

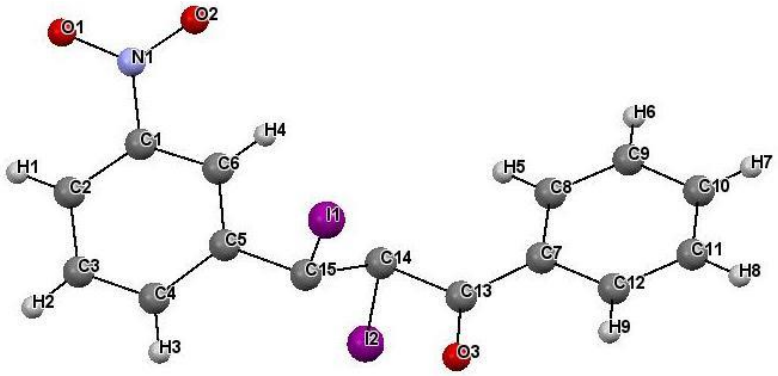
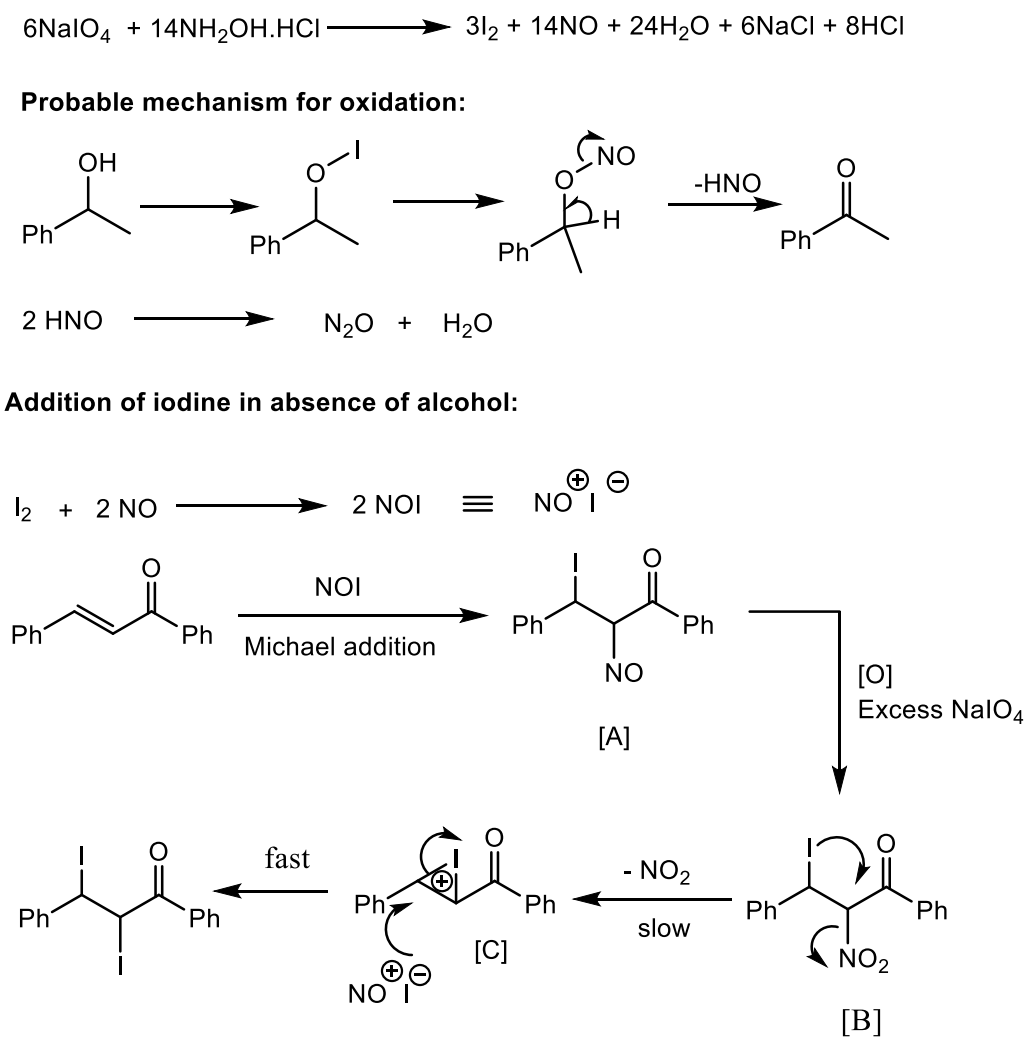


Figure 1. X-ray crystal structure of 2,3-diiodo-3-(3-nitro-phenyl)-1-phenylpropan-1-one (**2c**) with 30% probability.



Scheme 4. Probable mechanistic pathway.

The mechanism of this reaction has not been well investigated. We have suggested a probable mechanistic pathway for oxidation of alcohol (Scheme 4) to carbonyl compounds[24] and the preparation of β-iodo-β′-hydroxy ethers, β-iodo ethers, β-iodohydrin, and β-iodoacetoxy compounds using different reaction media (nucleophiles).[25] Again as suggested by Radner[26] we can suggest that in absence of alcohol the *in situ* generated iodine and NO may react to produce NOI, which may undergo simple Michael addition to the α,β-unsaturated carbonyl compound giving the vicinal iodonitroso compound [A]. This in presence of excess $NaIO_4$ or air undergoes oxidation to produce nitro compound [B]. Slow elimination of NO_2 produce an iodonium intermediate [C] followed by addition of iodide from NOI gives the diodo compound.

The structure of the product were well characterized by the spectral data and the X-ray crystallographic analysis of 2,3-diiodo-3-(3-nitro-phenyl)-1-phenyl-propan-1-one (**2c**) was performed to confirm the structure of the product as shown in Figure 1.[27]

Conclusions

In summary, we have observed that the combination of $NH_2OH{\cdot}HCl$ and $NaIO_4$ as a new and mild reagent for the synthesis of vicinal diiodo carbonyl compounds from *α,β*-unsaturated carbonyl compounds. To the best of our knowledge this is the first report to synthesize vicinal diiodo compounds of carbonyl compounds. The present procedure is also applicable for diiodination of nitrostyrene. The remarkable advantages of the present methodology are: (a) room temperature reaction; (b) easy operation; (c) good yields; (d) fast reaction; (d) transition metal-free; and (e) neutral reaction conditions. The extension of this methodology for the synthesis of a diiodo derivative on a gram-scale demonstrated the potentiality of industrial applications.

Experimental Section

General. ^1H NMR spectra was determined on a Bruker (300 & 400 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) and are referenced to tetramethylsilane (TMS) as internal standard and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants J were given in Hz. ^{13}C NMR spectra was recorded at 75 & 100 MHz in $CDCl_3$ solution. Melting points were determined using a locally made instrument (Science India, Kolkata). IR spectra were taken as KBr plates in a Shimazdu 8400S FTIR. Elemental analyses were done by a Perkin-Elmer auto analyzer. Mass spectra (2a) were recorded on a Q-Tof microTM (Waters Corporation) mass spectrometer by positive mode electro spray ionization process. TLC was done on silica gel coated glass slide (Merck, Silica gel G for TLC). Silica gel (60-120 mesh, SRL, India) was used for column chromatography. Petroleum ether refers to the fraction boiling in the range of 60-80°C unless otherwise mentioned. All solvents

were dried and distilled before use. Commercially available substrates were freshly distilled before the reaction. All reactions were executed using oven dried glassware.

General experimental procedure for the synthesis of vicinal diiodo compounds (2). A mixture of alkene (**1**, 1 mmol), $NaIO_4$ (2 mmol, 426 mg) in 2 mL of DCM was taken in an open round bottomed flask at room temperature and then $NH_2OH{\cdot}HCl$ (4 mmol, 276 mg) was added portion wise over 10 min. After completion (TLC), the reaction mixture was diluted with a 1:1 mixture of water/DCM (15 mL) and the DCM layer and washed with 10% (w/v) $Na_2S_2O_3$ (3 × 5ml). Then the combined organic layer was dried over anhydrous Na_2SO_4. Crude product was obtained by evaporation of solvent, which was purified by column chromatography using ethyl acetate-petroleum ether as eluent (1:20 to 1:10) to obtain the analytically pure product (**2**).

2,3-Diiodo-1,3-diphenylpropan-1-one (**2a**). White solid; yield: 388 mg (84%); mp 110-111 °C; IR (KBr): 3062, 2990, 1687, 1450 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.14-8.09 (m, 2 H), 7.85-7.35 (m, 7 H), 7.26 (d, *J* 8.8 Hz, 1 H), 5.88 (d, *J* 6.6 Hz, 1 H), 5.69 (d, *J* 5.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 192.64, 139.27, 134.10, 129.51, 129.46, 129.10, 128.90, 128.86, 128.76, 128.64, 128.58, 128.45, 128.18, 60.83, 29.51; HRMS (ESI) m/z: calcd for $C_{15}H_{12}I_2O$: 484.8875 $[M+Na]^+$; Found: 484.8875.

3-(4-Chlorophenyl)-2,3-diiodo-1-phenylpropan-1-one (2b). White solid; 401 mg (81%); mp 128-129 °C; IR (KBr): 3055, 2995, 1677, 1487, 1359 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.01-7.81 (m, 2 H), 7.68-7.35 (m, 7H), 5.82 (d, *J* 11.1 Hz, ½ H), 5.64 (d, *J* 11.1 Hz, ½ H), 5.46 (d, *J* 6 Hz, 1 H); ^{13}C NMR ($CDCl_3$,75 MHz,): δ = 192.18, 137.66, 135.55, 134.33, 132.63, 129.65, 129.19, 128.96, 128.45, 56.81, 28.95; Anal. Calcd for $C_{15}H_{11}ClI_2O$: C, 36.29; H, 2.23. Found: C, 36.22; H, 2.13%.

2,3-Diiodo-3-(3-nitrophenyl)-1-phenylpropan-1-one (2c). White solid; 416 mg (82%); mp 142-144 °C; IR (KBr): 3079, 1999, 1677, 1527, 1444 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.46-8.42 (m, 1H), 8.32-8.29 (m, 1H), 8.12-8.10 (m, 2H), 7.86-7.83 (m, 1H), 7.71-7.56 (m, 4H), 5.84 (d, *J* 10.8 Hz, 1 H), 5.76 (d, *J* 10 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 190.78, 141.54, 139.51, 138.62, 134.50, 129.96, 129.25, 128.94, 124.43, 123.52, 123.18, 59.27, 28.44; Anal. Calcd for $C_{15}H_{11}I_2NO_3$: C, 35.53; H, 2.19; N, 2.76%. Found: C, 35.45; H, 2.14; N, 2.71%.

2,3-Diiodo-1-(4-methoxyphenyl)-3-phenylpropan-1-one (2d). Light pink gummy mass; 394 mg (80%); IR (KBr): 3068, 2985, 1682, 1385 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, *J* 8.8 Hz, 2 H), 7.33-7.27 (m, 5 H), 6.88-6.85 (m, 2 H), 5.75 (d, *J* 11.2 Hz, 1 H), 5.54 (d, *J* 11.2 Hz, 1 H), 3.75 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 191.12, 164.34, 139.29, 129.39, 129.34, 129.15, 128.84, 128.79, 128.38, 128.10, 114.31, 60.94, 55.67, 29.32; Anal. Calcd for $C_{16}H_{14}I_2O_2$: C, 39.05; H, 2.87%. Found: C, 39.01; H, 2.80%.

2,3-Diiodo-3-phenylpropionic acid (2e). White solid; 333 mg (83%); mp 115-117 °C; IR (KBr): 3060, 3006, 1699, 1429 cm^{-1}; ^1H NMR ($CDCl_3$,300 MHz): δ = 10.86 (br, 1 H), 7.52-7.37 (m, 5 H), 5.35 (d, *J* 12 Hz, 1 H), 4.89 (d, *J* 12 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 175.22, 138.05, 128.94, 128.78, 128.39, 128.05, 127.75, 61.35, 24.72; Anal. Calcd for $C_9H_8I_2O_2$: C, 26.89; H, 2.01%. Found: C, 26.82; H, 1.97%.

2,3-Diiodobutyric acid (2f). Light grey gummy mass; 275 mg (81%); IR (KBr): 3080, 3024, 2987, 1712, 1427 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 10.17 (br, 1 H), 4.48-4.32 (m, 2 H), 1.79 (d, *J* 12 Hz, 3 H); ^{13}C NMR ($CDCl_3$,75 MHz): δ = 175.39, 55.63, 25.83, 24.63; Anal. Calcd for $C_4H_6I_2O_2$: C, 14.13; H, 1.78. Found: C, 14.07; H, 1.72%.

Methyl 2,3-diiodo-3-phenylpropionate (2g). White gummy mass; 341 mg (84%). IR (KBr): 3006, 2948, 1733, 1442 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.45-7.35 (m, 5 H), 5.35 (d, *J* 11.7 Hz, 1 H), 4.84 (d, *J* 11.7 Hz, 1 H), 3.87 (s, 3 H); ^{13}C NMR($CDCl_3$,75 MHz): δ = 169.72, 138.20, 129.42, 128.73, 128.01, 61.72, 53.29, 24.92; Anal. Calcd. for $C_{10}H_{10}I_2O_2$: C, 28.87; H, 2.42. Found: C, 28.81; H, 2.37%.

1,2,4,5-Tetraiodo-1,5-diphenylpentan-3-one (2h). Light grey solid; 608 mg (82%); mp. 105-106 °C; IR (KBr): 3062, 3026, 2997, 1703, 1452, 1380 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.46-7.37 (m, 10 H), 5.60-5.52 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 190.56, 139.17, 129.31, 128.74, 128.14, 58.90, 33.30; Anal. Calcd for $C_{17}H_{14}I_4O$: C, 27.52; H, 1.90. Found: C, 27.43; H, 1.85 %.

(1,2-Diiodo-2-nitroethyl)benzene (2i). Light yellow gummy mass (306 mg, 76%); IR (KBr): 3077, 1993, 1675, 1522, 1453 cm^{-1}; ^1H NMR ($CDCl_3$,400 MHz): δ = 7.88-7.39 (m, 5 H), 6.51 (d, *J* 12 Hz, 1 H), 5.55 (d, *J* 12 Hz, 1 H); ^{13}C NMR ($CDCl_3$,100 MHz): δ = 139.68, 128.82, 128.59, 126.42, 70.74, 33.64; Anal. Calcd for $C_8H_7I_2NO_2$: C, 23.85; H, 1.75; N, 3.48. Found: C, 23.81; H, 1.68; N, 3.42 %.

Typical procedure for the gram-scale synthesis of 2,3-diiodo-3-(3-nitrophenyl)-1-phenyl-propan-1-one (2c). In a typical experimental procedure a mixture of (*E*)-3-(3-nitrophenyl)-1-phenylprop-2-en-1-one (20 mmol, 5.06 g), $NaIO_4$ (40 mmol, 8.52 g) in 40 mL of DCM was taken in an open 100 mL round bottomed flask at room temperature and then $NH_2OH{\cdot}HCl$ (80 mmol, 5.52 g) was added by portion for 20 min. After completion (TLC), the reaction mixture was diluted with a 1:1 mixture of water/DCM (100 mL) and the DCM layer was collected washed with 10% (w/v) $Na_2S_2O_3$ (3 × 15 mL). Then the combined organic layer was dried over anhydrous Na_2SO_4. Crude product was obtained by evaporation of solvent, which was purified by column chromatography using ethyl acetate-petroleum ether as eluent (1:10) to obtain the analytically pure product as a white solid.

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