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Preparation and X-ray Structures of 3-[Bis(trifluoroacetoxy)iodo]benzoic Acid and 3-[Hydroxy(tosyloxy)iodo]benzoic Acid: New Recyclable Hypervalent Iodine Reagents

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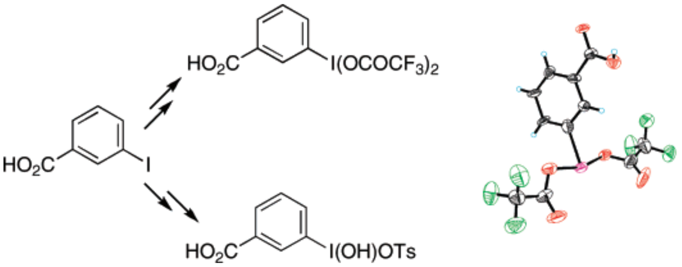

Preparation, structural characterization, and reactivity of 3-[bis(trifluoroacetoxy)iodo]benzoic acid and 3-[hydroxy(tosyloxy)iodo]benzoic acid, new recyclable iodine(III) reagents derived from 3-iodosylbenzoic acid, are described. The reduced form of these reagents, 3-iodobenzoic acid, can be easily recovered from the reaction mixtures using ion-exchange resin or basic aqueous workup followed by acidification with HCl.

Hypervalent iodine reagents have emerged as reagents of choice for various synthetically useful oxidative transformations.[1] The most widely used reagents, such as, iodosylbenzene, (diacetoxy)iodobenzene, [bis(trifluoroacetoxy)iodo]benzene and [hydroxy(tosyloxy)iodo]benzene are based on the oxidized forms of iodobenzene. The reactions of these reagents with organic substrates lead to iodobenzene as the byproduct, which is difficult to recover and reuse because of the high volatility and solubility in organic solvents. Several research groups have tried to improve the iodobenzene-based hypervalent iodine reagents by developing their polymer-supported analogues, such as, poly(diacetoxyiodo)styrene, poly[bis(trifluoroacetoxy)iodo]styrene, poly[hydroxy(tosyloxy)iodo]styrene), etc.[2] Despite the utility of the polymer-supported reagents, they still have several drawbacks. These reagents require a multistep preparation, they have lower reactivity compared to that of the corresponding monomeric analogues, and moreover, the repeated use of these polymers leads to significant degradation due to the benzylic oxidation of the polystyrene chain. The other previously reported approaches to recyclable hypervalent iodide reagents involve non-polymeric molecular species,[3] which require multistep syntheses or employ fluorous alkyl iodides and fluorous solvents for separation of products.[4]

Recently, tagging strategies for reagents and catalysts have widely been investigated that allow easy purification by means of specific phase separation or scavenging.[5] We have found that 3-iodosylbenzoic acid (which has a polymeric structure **2**,[6] see Scheme 1) is an excellent oxygenating reagent whose reduced form, 3-iodobenzoic acid **1**, can be removed at the end of the reaction by treatment with anionic-exchange resin or by addition of NaHCO$_3$ and can be easily recycled.[7] Likewise, 3-(dichloroiodo)benzoic acid is an excellent chlorinating reagent that can be similarly recycled via 3-iodobenzoic acid.[8] In contrast to the previously reported protocols,[2−4] hypervalent iodine reagents derived from 3-iodobenzoic acid are inexpensive and readily available compounds that can be easily recovered from the reaction mixture.

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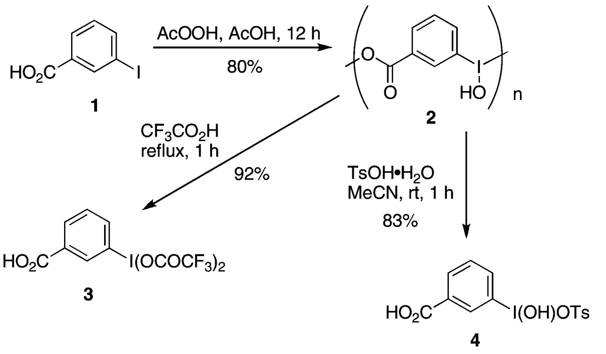
SCHEME 1. Preparation of 3-Iodosylbenzoic Acid 2 and Its Derivatives 3 and 4



We report the preparation and X-ray crystal structure of two new recyclable non-polymeric hypervalent iodine reagents derived from 3-iodobenzoic acid, namely, 3-[bis(trifluoroacetoxy)iodo]benzoic acid, **3**, and 3-[hydroxy(tosyloxy)iodo]benzoic acid, **4**. Compounds **3** and **4** were conveniently prepared in high yield by treatment of 3-iodosylbenzoic acid, **2**,[7] with trifluoroacetic acid or *p*-toluenesulfonic acid, respectively (Scheme 1).

Products **3** and **4** were isolated as white, stable, microcrystalline compounds and were analyzed by NMR spectroscopy, elemental analysis, and X-ray crystallography. Molecular structures of **3** and **4** are presented in Figures 1 and 2.

It is interesting to note that the presence of a meta carboxylic group does not have any noticeable effect on the molecular geometries of products **3** and **4** which, in general, are similar to the previously reported X-ray crystal structures of [bis(trifluoroacetoxy)iodo]benzene[9] and [hydroxy(tosyloxy)iodo]benzene.[10] Both structures **3** and **4** have a distorted T-shaped geometry at the iodine(III) center. In the molecule of trifluoroacetate **3** intramolecular I•••O interactions with the carboxylate oxygens O(4) and O(5) are observed with distances I(1)•••O(5) 3.146 Å and I(1)•••O(4) 3.030 Å. In addition to the five intramolecular interactions, an intermolecular coordination of an iodine atom to one of the carboxylic oxygens of the neighboring molecule was also found with a distance of 3.023 Å. The overall geometry of the iodine coordination sphere in **3** could be represented as a distorted octahedron, similar to the structure of [bis(trifluoroacetoxy)iodo]benzene.[9]

The I−OTs bond distance in tosylate **4**, (2.437 Å), is significantly longer than the I−OH bond distance of 1.954 Å, which is indicative of some ionic character of this compound. Bond distances and angles at the iodine(III) center in **4** are very close to the respective structural parameters previously reported for [hydroxy(tosyloxy)iodo]benzene.[10] In addition to the three intramolecular bonds, a weaker intermolecular coordination of iodine atom to one of the sulfonyl oxygens of the neighboring molecule is found with a distance of 2.931 Å. No intermolecular interaction involving meta carboxylic group can be found in both molecules **3** and **4**, which is in sharp contrast with the polymeric structure of 3-iodobenzoic acid **2**.[6] The monomeric character of **3** and **4** leads to the improved solubility and higher reactivity compared those of to 3-iodobenzoic acid **2**.

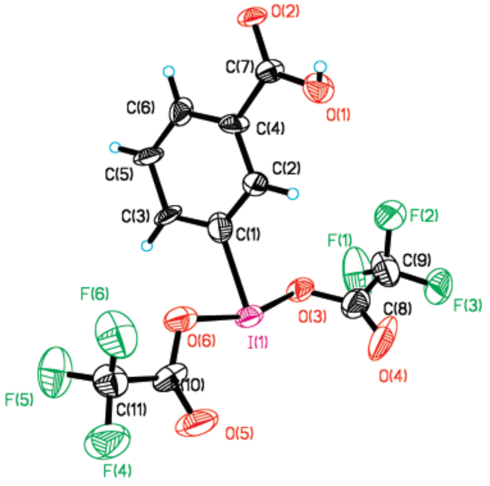


FIGURE 1. Perspective view of one of five crystallographically independent molecules 3-[bis(trifluoroacetoxy)iodo]benzoic acid, **3**, with 50% ellipsoid. Selected distances [Å] and angles [deg]: I(1)−C(1) 2.083, I(1)−O(3) 2.149, I(1)−O(6) 2.186, I(1)•••O(5) 3.146, I(1)•••O(4) 3.030; C(1)−I(1)−O(3) 83.26, O(3)−I(1)−O(6) 163.85.

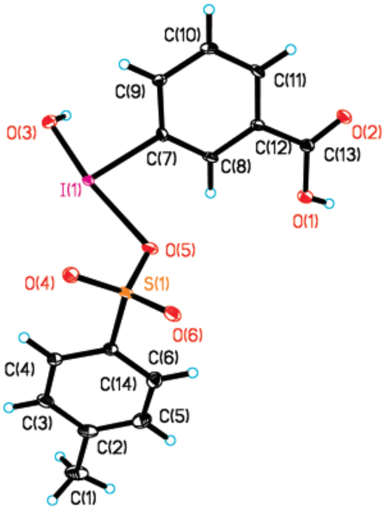


FIGURE 2. X-ray crystal structure of 3-[hydroxy(tosyloxy)iodo]benzoic acid, **4**, with 50% ellipsoid. Selected distances [Å] and angles [deg]: I(1)−C(7) 2.105, I(1)−O(3) 1.954, I(1)−O(5) 2.437; O(3)−I(1)−C(7) 92.21, O(3)−I(1)−O(5) 172.02.

As expected from the structural similarity, the reactivity pattern of **3** and **4** is similar to [bis(trifluoroacetoxy)iodo]benzene and [hydroxy(tosyloxy)iodo]benzene, both of which belong to the most important and widely used representatives of hypervalent iodine reagents.[1] The oxidative properties of reagents **3** and **4** were evaluated in the most typical reactions previously reported for $PhI(OCOCF_3)_2$ and PhI(OH)OTs, such as oxidation of sulfides,[3a,11] oxidative iodination of arenes,[12] α-tosyloxylation of ketones,[2g,3a,13] and Hofmann-type rearrangement[3a,14] (Scheme 2). The products of these reactions (Scheme 2) were conveniently separated from the byproduct, 3-iodobenzoic acid **1**, by simple treatment with ion-exchange resin IRA-900. 3-Iodobenzoic acid **1** can easily be regenerated from IRA

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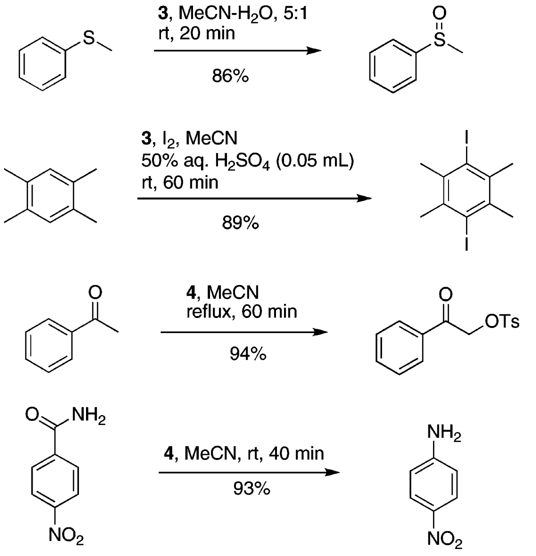
SCHEME 2. Representative Reactions of Reagents 3 and 4



900 resin by treatment with aqueous HCl and can be reoxidized to reagent **2** without additional purification.[7] An alternative procedure for product separation involves basic aqueous workup followed by acidification with HCl.[8]

In conclusion, we have reported the preparation, X-ray structural characterization, and useful reactivity of 3-[bis(trifluoroacetoxy)iodo]benzoic acid, **3**, and 3-[hydroxy(tosyloxy)iodo]benzoic acid, **4**, new recyclable iodine(III) reagents derived from 3-iodosylbenzoic acid.

Experimental Section

Additional experimental details can be found in the Supporting Information.

3-[Bis(trifluoroacetoxy)iodo]benzoic Acid (3). A mixture of 3-iodosylbenzoic acid **1** (0.264 g, 1 mmol) and trifluoroacetic acid (2 mL) was refluxed for 1 h. After cooling to room temperature, the resulting solution was concentrated in vacuum to the volume of about 1 mL, and then dichloromethane (2 mL) was added to this solution. The resulting mixture was heated to boiling point and then cooled to 0 °C; the precipitate was filtered, washed with cold dichloromethane, and dried to afford 0.436 g (92%) of product **3** in the form of white crystals, mp 125−127 °C (with decomposition). ^{1}H NMR ($CDCl_3$−CF_3CO_2H, 2:3): δ 9.05 (s), 8.57 (d, J = 8 Hz, 1H), 8.54 (d, J = 8 Hz, 1H), 7.84 (t, J = 8 Hz, 1H). ^{13}C NMR ($CDCl_3$−CF_3CO_2H, 2:3): δ 170.6, 163.0 (q, overlapping with signal from CF_3CO_2H), 141.1, 137.7, 136.1, 133.0, 132.9, 122.8, 115.0 (q, overlapping with signal from CF_3CO_2H). Anal. Calcd for $C_{11}H_5F_6IO_6$: C, 27.87; H, 1.06. Found: C, 27.95; H, 0.97.

3-[Hydroxy(tosyloxy)iodo]benzoic Acid (4). A mixture of 3-iodosylbenzoic acid **1** (0.264 g, 1 mmol) and *p*-TsOH•H_2O (0.38 g, 2 mmol) in acetonitrile (2 mL) was stirred at room temperature for 1 h. The resulting precipitate was filtered, washed with cold dichloromethane (2 mL), and dried to afford 0.362 g (83%) of product **4** in the form of white crystals, mp 132−134 °C (with decomposition). IR (KBr): 3240, 1687, 1235, 1100 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.69 (s), 8.42 (d, J = 8 Hz, 1H), 8.19 (d, J = 8 Hz, 1H), 7.45 (t, J = 8 Hz, 1H), 7.46 (d, J = 8 Hz, 2H), 7.11 (d, J = 8 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 165.7, 145.6, 138.1, 137.7, 134.6, 133.2, 132.7, 131.4, 128.1, 122.5, 123.3, 20.8. Anal. Calcd for $C_{14}H_{13}IO_6S$: C, 38.55; H, 3.00. Found: C, 38.92; H, 2.87.

X-ray Crystal Structure Determination of 3 and 4. The diffraction data were collected with synchrotron radiation (λ = 0.80000 Å) at the Wiggler Beamline 4A, Pohang Accelerator Laboratory. Data reduction and adsorption correction were performed with HKL2000 package. The structures were solved by direct methods and refined by full-matrix least-squares method with SHELXTL package. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions. Crystal data for **3**: $C_{11}H_4O_6F_6I$, M = 473.04, triclinic, space group $P\bar{1}$ (No. 2), a = 14.302(3) Å, b = 15.142(3) Å, c = 17.101(3) Å, α = 97.53(3)°, β = 101.25(3)°, γ = 90.66(3)°, V = 3598.3(12) Å^3, Z = 10, T = 90 K, $\mu(\lambda = 0.80000$ Å$)$ = 3.154 mm^{-1}, d_{calc} = 2.183 g/cm^3, 10346 reflections measured, 10346 unique, R1 = 0.0755, wR2 = 0.2513 ($I > 2\sigma(I)$), R1 = 0.1099, wR2 = 0.2837 (all data), GOF = 0.753. Crystal data for **4**: $C_{14}H_{13}O_6SI$, M = 436.20, monoclinic, space group $P2_1/c$ (No. 14), a = 17.534(3) Å, b = 12.134(2) Å, c = 7.166(1) Å, β = 99.15(3)°, V = 1505.2(5) Å^3, Z = 4, T = 90 K, $\mu(\lambda = 0.80000$ Å$)$ = 3.114 mm^{-1}, d_{calc} = 1.925 g/cm^3 5316 reflections measured, 3089 unique (R_{int} = 0.0698), R1 = 0.0476, wR2 = 0.1327 ($I > 2\sigma(I)$), R1 = 0.0479, wR2 = 0.1332 (all data), GOF = 1.015. For further details on crystal structures see the Crystallographic Information File (deposited as Supporting Information).

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Supporting Information Available: Details of the experimental procedures, spectroscopic data of the reaction products, and X-ray data for the compounds **3** and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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