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Preparation and Chemistry of Stable Azidoiodinanes: 1-Azido-3,3-bis(trifluoromethyl)-3-(1*H*)-1,2-benziodoxol and 1-Azido-1,2-benziodoxol-3-(1*H*)-one

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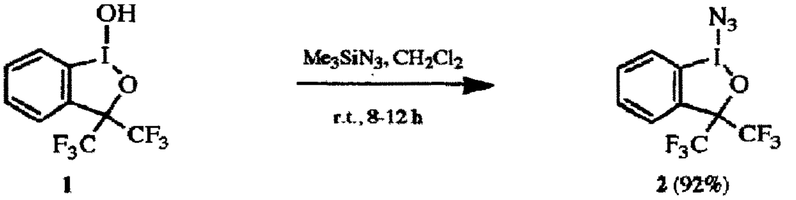
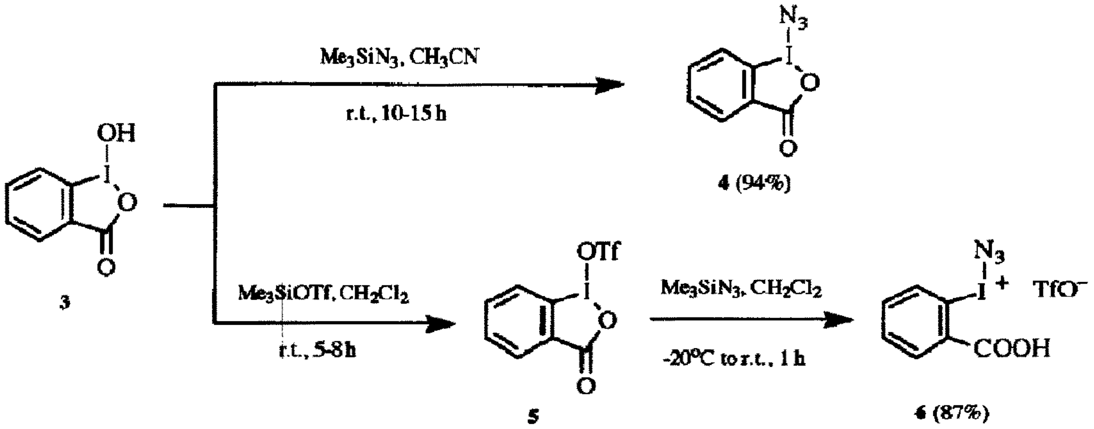
Abstract: Azidoiodinanes **2,4,6** can be prepared from benziodoxols **1,3** and trimethylsilyl azide in the form of stable, crystalline compounds. These compounds are potentially useful reagents for electrophilic azidonation of organic substrates. For example, reaction of azide **6** with cyclohexene affords 2-azidocyclohexanone **7** in moderate yield.

The combination of a hypervalent iodine compound and trimethylsilyl azide, PhIO/TMSN$_3$ or PhIX$_2$/TMSN$_3$, is a well-known, efficient reagent for the introduction of azido function into organic molecules.[1,2] Azidoiodinanes, PhI(N$_3$)X or PhI(N$_3$)$_2$, were proposed as reactive intermediates in the azidonation reactions.[2] However, attempts to isolate these species always resulted in fast decomposition at -25 to 0°C with the formation of iodobenzene and dinitrogen.[2,3] Low stability of the reported PhIO/TMSN$_3$ reagent combination restricts its practical application only to low temperature reactions with the most reactive nucleophilic organic substrates, such as alkenes, amines, and enol ethers.[1,2]

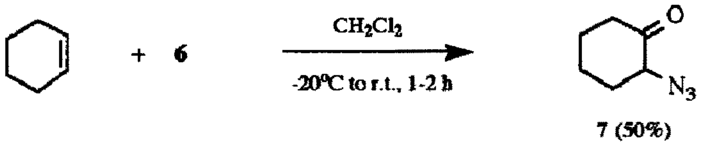
In the present communication we wish to report the preparation of stable azidoiodinanes **2,4,** and **6** from readily available benziodoxols **1** and **3**. Azides **2** and **4** were synthesized in one step by the reaction of compounds **1** or **3** with trimethylsilyl azide in dichloromethane.[4,5] Mixed azidotriflate **6** was prepared by a two-step reaction sequence.[6] At the first step, benziodoxol **3** was treated with trimethylsilyl triflate to generate an intermediate benziodoxol triflate **5**[7] which was used for further transformation in situ. At the second step, trimethylsilyl azide was added at low temperature to give a yellow precipitate of **6**. All three azidoiodinanes (**2,4,6**) were isolated as thermally stable crystalline solids with melting/decomposition points above 127°C. Specially performed thermal and shock tests did not reveal any explosive properties for crystalline products **2** and **6**; however, azidoiodinane **4** decomposed with explosion at 138-139°C. We recommend to follow standard precautions of work with these potentially dangerous azides.

Azidoiodinanes **2,4,** and **6** were identified by spectral data and elemental analyses.[4-6] Specifically, IR spectra of all three compounds displayed a very intense peak of azido function at 2046, 2048 and 2066 cm^{-1}, respectively. ^1H and ^{13}C NMR spectra showed signals and splitting patterns typical of *o*-substituted benzene rings and were consistent with the proposed structures. In our schemes, compounds **2** and **4** are presented as conventional, cyclic benziodoxols. However, an open zwitterionic structure for **2** and **4** cannot be excluded because available X-ray data on 2-iodosylbenzoic acid and its derivatives indicate that the I-O distance in the benziodoxol ring is significantly longer than the computed covalent single bond length.[8]





Preliminary studies indicate that compounds **2**, **4** and **6** react with alkenes and silyl enol ethers with the formation of organic azides, similarly to previously reported PhIO/TMSN$_3$ and PhIX$_2$/TMSN$_3$ systems. As a representative example, azidoiodinane **6** reacts with cyclohexene in CH_2Cl_2 at -20 °C to give 2-azidocyclohexanone **7** as the major product. This reaction is similar to the previously reported conversion of cyclohexene to 2-azidocyclohexanone by the action of PhI(OAc)$_2$/TMSN$_3$.[2d]



Recently Magnus and co-workers reported application of the reagent system *o*-iodosyl benzoic acid/TMSN_3 in CH_2Cl_2 at reflux conditions for azidonation of amides.[2a] Considering our preparation of azidoiodinane **4** under similar conditions, it is most likely that azide **4** is the actual reagent in this reaction.

In conclusion, we have prepared and isolated as individual, stable compounds azidoiodinanes **2**,**4**, and **6**. These compounds are potentially useful reagents for electrophilic azidonation of electron rich organic substrates.

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4. (a) Preparation of **2**: To a stirred mixture of 1-hydroxy-3,3-bis(trifluoromethyl)-3-(1*H*)-1,2-benziodoxol 1^{3b} (0.5 g, 1.3 mmol) in dry CH_2Cl_2 (20 ml), trimethylsilylazide (0.35 ml, 2.6 mmol) was added under nitrogen at room temperature. The reaction mixture was stirred for 18 hrs, then the resulting yellow solution was evaporated in vacuum to give a pale yellow microcrystalline residue of azide **2**; yield 0.49 g (92%), mp 135-137 ^{o}C (dec.); IR (CCl_4): 3082 (Ar), 2046 (N_3), 1266, 1186, 1141, 1111, 1041 (CF_3) cm^{-1}; ^1H NMR ($CDCl_3/CD_3CN$, 10:1): δ 7.9 – 7.65 (m, C_6H_4); ^{13}C NMR ($CDCl_3/CD_3CN$, 10:1): δ 133.65, 131.48, 131.39, 131.29, 130.27, 127.70 (Ar), 120.82 (q, J = 318 Hz, CF_3), 113.77.

Anal: Calc. for $C_9H_4IF_6ON_3$: C, 26.30; H, 0.98. Found: C, 27.04; H, 1.14. (b) Benziodoxol **1** was prepared by oxidation of 2-(2-iodophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol[3c] with peracetic acid; (c) Perozzi, E.F.; Michalak, R.S.; Figuly, G.D.; Stevenson III, W.H.; Dess, D.B.; Ross, M.R.; Martin, J.C. *J. Org. Chem.* **1981**, *46*, 1049.

5. Preparation of **4**: To a stirred mixture of 2-iodosobenzoic acid **3** (0.53 g, 2 mmol) in dry acetonitrile (20 ml), trimethylsilylazide (0.53 ml, 4 mmol) was added under nitrogen at room temperature. The reaction mixture was stirred for 10-15 h until the formation of a clear, pale yellow solution. The resulting solution was evaporated in vacuum to give slightly yellow microcrystalline residue of azide **4**, which was washed with anhydrous ether and dried in vacuum; yield 0.54 g (94%), mp 138-139 ^oC (expl.); IR (CCl_4): 3065 (Ar), 2048 (N_3), 1643 (C=O) cm^{-1}; ^1H NMR ($CDCl_3/CD_3CN$, 10:1): δ 8.19 (d, 1H, J = 8 Hz), 8.03 (m, 2H, J = 8 Hz), 7.77 (t, 1H, J = 8 Hz); ^{13}C NMR ($CDCl_3/CF_3COOH$, 20:1): δ 171.11 (C=O), 137.28, 128.69, 126.69, 126.57, 118.84, 117.66 (Ar). Anal: Calc. for $C_7H_4IO_2N_3$: C, 29.09; H, 1.39. Found: C, 29.40; H, 1.48.
6. Preparation of **6**: To a stirred mixture of 2-iodosobenzoic acid (0.53 g, 2 mmol) in dry CH_2Cl_2 (20 ml), trimethylsilyltriflate (0.43 ml, 2.2 mmol) was added under nitrogen at room temperature. The resulting mixture turned into a clear solution after 10-20 min of stirring and then yellow precipitate formed. After 5-8 h of stirring, the reaction mixture was cooled to -20 ^oC and trimethylsilylazide (0.53 ml, 4 mmol) was added. The reaction mixture was stirred for 10-15 min until the formation of a pale yellow precipitate of the product **6**. The precipitate was filtered under nitrogen, washed with dry CH_2Cl_2 and dried in vacuum; yield 0.76 g (87%), mp 127-129 ^oC (dec.).; IR (CCl_4): 3074 (Ar), 2066 (N_3), 1682 (C=O), 1268, 1170, 1032 (OTf) cm^{-1}; ^1H NMR ($CDCl_3/CF_3COOH$, 20:1): δ 8.40 (d, 1H, J = 8 Hz), 8.05 (m, 2H, J = 8 Hz), 7.90 (t, 1H, J = 8 Hz). Anal: Calc. for $C_8H_5IF_3O_5N_3 \cdot H_2O$: C, 21.01; H, 1.54. Found: C, 21.20; H, 1.46.
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