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1-Cyano-3-(1*H*)-1,2-benziodoxols: Stable Cyanoiodinanes and Efficient Reagents for Direct *N*-Alkyl Cyanation of *N,N*-Dialkylarylamines

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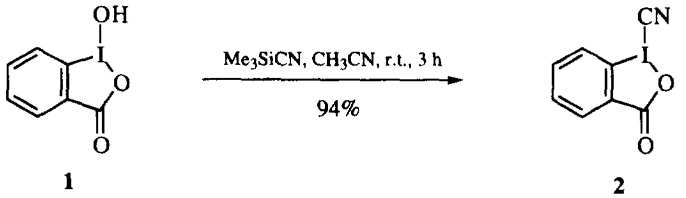
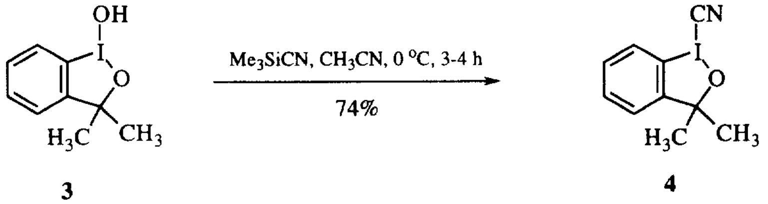
Abstract: Cyanobenziodoxols **2** and **4** can be prepared from benziodoxols **1** or **3** and cyanotrimethylsilane in the form of stable, crystalline compounds. Cyanobenziodoxol **2** reacts with *N,N*-dimethylarylamines under mild conditions to afford *N*-(cyanomethyl)-*N*-methylarylamines **6** in excellent yields.

The cyano derivatives of polyvalent iodine have found synthetic application as efficient iodonium transfer reagents useful in the synthesis of various iodonium salts.[2] Three structural types of cyanoiodinanes are known: [(dicyano)iodo]benzene, $PhI(CN)_2$,[3a] (dicyano)iodonium triflate, $(CN)_2IOTf$,[2c,3c] and [cyano(organosulfonyloxy)iodo]arenes, $ArI(CN)OSO_2R$.[2a,b,3b,d,e] [(Dicyano)iodo]benzene and (dicyano)iodonium triflate are thermally unstable and air-sensitive; however, $(CN)_2IOTf$ can be used in situ for the preparation of bis(heteroaryl)iodonium salts by the iodonium transfer reaction with the respective stannylated heteroarenes.[2c,3b] [Cyano(organosulfonyloxy)iodo]arenes have relatively higher stability, and PhI(CN)OTf is especially useful reagent in the synthesis of alkynyliodonium and alkenyliodonium salts.[2a,b] In this communication we wish to report the preparation and chemical reactivity of a new structural type of stable cyanoiodinanes - derivatives of benziodoxols.[4,5]

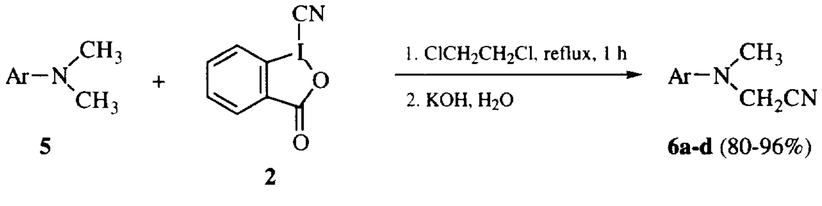
Cyanobenziodoxols **2** and **4** can be conveniently prepared in one step by the reaction of cyanotrimethylsilane with the commercial 2-iodosobenzoic acid **1** or 1-hydroxy-3,3-dimethyl-3-(1*H*)-1,2-benziodoxol **3**, respectively.[6]





Both adducts (**2** and **4**) were isolated as thermally stable, white, microcrystalline solids and identified by spectral data and elemental analyses.[6] Particularly characteristic were ^{13}C NMR spectra displaying all the respective signals of carbon skeletons, and the cyano carbons at $\delta = 87.8$ ppm for **2** and at $\delta = 97.8$ ppm for **4**. In the case of previously reported cyanoiodinanes, signals of the cyano carbons were observed at: $\delta \approx 69\text{-}71$ ppm for ArI(CN)OTf;[3b,e] $\delta = 124.75$ ppm for $PhI(CN)_2$;[3a] and at $\delta = 32.1$ ppm for $(NC)_2IOTf$.[3c] The IR absorption of the cyano group was observed at 2161 cm^{-1} for **2**, and at 2164 cm^{-1} for **4**, which is very similar to the IR of the previously reported cyanoiodinanes.[3]

Preliminary study of chemical reactions of cyanobenziodoxols **2** and **4** indicates that their reactivity pattern is different from the previously reported cyanoiodonium salts.[2,3] In particular, our attempt to use these cyanides as iodonium transfer reagents in reactions with stannylated alkynes was not successful and did not lead to the formation of the respective alkynyliodonium derivatives. Further investigation showed that chemical reactivity of cyanobenziodoxols **2** and **4** is generally similar to that of azidoiodinanes, which have been found to be efficient radical azidonating reagents.[8] Analogously to azidoiodinanes, cyanobenziodoxols **2** and **4** can serve as efficient *cyano* transfer reagents toward *N*,*N*-dialkylarylamines. In a typical experiment, reagent **2** reacts with *N*,*N*-dimethylanilines **5** in dichloroethane at reflux to afford the respective *N*-cyanomethyl-*N*-methylanilines **6** in excellent yield.[9] Products of this reaction (**6a-d**) can be easily separated from the side product, 2-iodobenzoic acid, by washing the reaction mixture with an aqueous, basic solution.



6a: Ar = Ph (96%), 6b: Ar = 4-BrC_6H_4 (80%), 6c: Ar = 4-MeC_6H_4 (87%), 6d: Ar = 1-naphthyl (85%)

In conclusion, we have prepared and isolated as individual, stable compounds cyanobenziodoxols **2** and **4**. These compounds are potentially useful reagents for the direct cyanation of *N*,*N*-dialkylarylamines under mild conditions.

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6. **1-Cyano-1,2-benziodoxol-3-(1*H*)-one (2)**. Cyanotrimethylsilane (0.785 ml, 5.886 mmoles) was added to a stirred suspension of 2-iodosylbenzoic acid **1** (0.777 g, 2.943 mmoles) in dry CH_3CN (20 ml) under nitrogen at room temperature. The reaction mixture was additionally stirred for 3 hrs until the formation of a clear, colorless solution. This solution was cooled to -18°C and kept at this temperature for 2 hrs until a white microcrystalline precipitate formed. The precipitate was filtered,

washed with anhydrous CH_2Cl_2 (5 ml) and dried in vacuo to afford analytically pure product **2**; yield 0.755 g (94%), mp 173-175°C (dec.); IR (CCl_4): 3090 (Ar), 2161 (CN), 1685, 1632 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 8.27 (d, 1H, J = 8 Hz), 8.10 (d, 1H, J = 8 Hz), 7.98 (t, 1H, J = 8 Hz), 7.86 (t, 1H, J = 8 Hz); ^{13}C NMR (DMSO-d_6): δ 166.7 (C=O), 136.4, 132.0, 131.8, 130.1, 127.7, 117.4 (Ar), 87.8 (CN). Anal: Calc. for $C_8H_4INO_2{\bullet}0.5H_2O$: C, 34.07; H 1.79; N, 4.97. Found: C, 33.98; H, 1.76; N, 4.91.

1-Cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxol (4). To a stirred solution of 1-hydroxy-3,3-dimethyl-3-(1*H*)-1,2-benziodoxol[7] **3** (0.200 g, 0.72 mmol) in dry CH_3CN (15 ml), cyanotrimethylsilane (0.15 ml, 1.12 mmol) was added under nitrogen at 0°C. After stirring 3-4 h, the solvent was evaporated. The resulting dark orange oil was recrystallized from ether-hexane to afford analytically pure product **4**; yield 0.152 g (74%), mp 97-101°C; IR (CCl_4): 2964 (Ar), 2924, 2164 (CN), 1558, 1458, 1438, 1358, 1250, 1218, 1154, 1110, 1002, 954 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.06 (m, 1H), 7.58 (m, 2H), 7.33 (m, 1H), 1.49 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 147.97, 131.45, 130.67, 128.08, 126.66, 111.36 (Ar), 97.79 (CN), 80.13 ($\underline{C}(CH_3)_2$), 30.03 ($C(\underline{C}H_3)_2$) Anal: Calc. for $C_{10}H_{10}ION$: C, 41.84; H, 3.51. Found: C, 41.52; H, 3.64.

7. For the preparation of compound **3** see: Amey, R.L.; Martin, J.C. *J. Org. Chem.* **1979**, *44*, 1779.
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9. **Typical Procedure for Cyanation of *N,N*-Dimethylarylamines with Cyanobenziodoxol 2**: To a stirred mixture of cyanobenziodoxol **2** (0.225 g, 0.824 mmol) in dry 1,2-dichloroethane (20 ml) *N,N*-dimethylaniline (0.099 g, 0.824 mmol) was added under nitrogen at room temperature. The reaction mixture was then refluxed for 1 hr, then the resulting solution was washed with 0.5 M aqueous KOH (2 x 20 ml) and water (20 ml), and evaporated in vacuum to give *N*-cyanomethyl-*N*-methylaniline **6a** as a clear oil; yield 0.115 g (96%); IR (neat): 2220 (CN); ^1H NMR ($CDCl_3$): δ 7.0 (m, 5H, Ph), 4.23 (s, 2H, CH_2); 2.95 (s, 3H, CH_3); MS (EI, 70 eV): m/z (%) 146 (100), M^+. Products **6b-d** were prepared similarly and identified by their IR, NMR, and mass-spectra.

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