

Structure and Chemistry of Acetoxybenziodazole. Acid-Catalyzed Rearrangement of Benziodazoles to 3-Iminobenziodoxoles

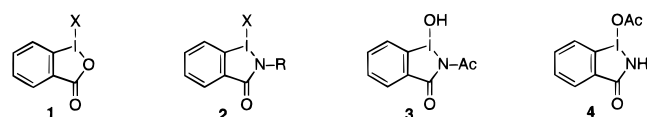
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The five-membered iodine–oxygen heterocycles, benziodoxoles (**1**), have recently attracted significant interest due to their excellent catalytic activity in the cleavage of toxic phosphates and several useful applications as reagents for organic synthesis.¹ The analogous iodine–nitrogen heterocycles, benziodazoles (**2**), have received much less attention.^{2–6} The most important and readily available is the acetate derivative of benziodazole. In particular, Moss and co-workers have found that acetoxybenziodazole has a minimal catalytic activity in the cleavage of a model phosphotriester under basic conditions.³ Acetoxybenziodazole was first prepared in 1965 by peracetic oxidation of 2-iodobenzamide.² Based on the IR spectroscopy, the authors² assigned the structure of *N*-acetyl-1-hydroxy-3-(1*H*)-1,2-benziodazole-3-one (**3**) for this compound. Structure **3** was also adopted in the more recent studies.^{3–5}



In this paper, we report the result of the X-ray analysis of acetoxybenziodazole, which is consistent with structural representation **4**, but not **3**, as well as some chemistry of this compound, including novel rearrangement of benziodazoles to 3-iminobenziodoxoles.

Compound **4** was prepared by oxidation of 2-iodobenzamide with peracetic acid according to the previously reported procedure.^{2,3} The infrared spectrum of our sample was in good agreement with literature data.^{2,3} In particular, the IR showed a broad absorption band centered at 3100 cm⁻¹, which was previously assigned to the hydroxyl group in structure **3**,² and two carbonyl bands at 1661 and 1610 cm⁻¹. Elemental analysis and NMR spectra of our sample were consistent with both alternative structures **3** and **4**, so we carried out X-ray analysis for a reliable structural assignment.^{7a} Suitable crystals were obtained from a solution in acetic acid at room temperature in the form of a solvate with one molecule of AcOH. The crystals readily lost solvent upon standing. The X-ray crystal structure of **4**·AcOH is shown in Figure 1. The structural data revealed the expected T-shaped geometry for hypervalent iodine with a N–I–O bond angle of 162.1(2)°. The lengths of the bonds to

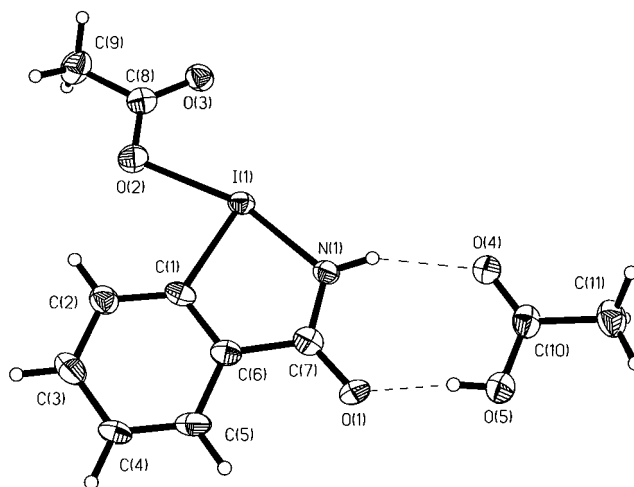


Figure 1. X-ray structure of **4**·AcOH. Selected bond lengths (Å): I(1)–N(1), 2.101(5); I(1)–C(1), 2.106(6); I(1)–O(2), 2.234(4); C(7)–N(1), 1.338(7); C(7)–O(1), 1.246(8); H–O(5), 0.84; H–N(1), 0.88. Selected bond angles (deg): N(1)–I(1)–C(1), 78.7(2); C(1)–I(1)–O(2), 83.4(2); N(1)–I(1)–O(2), 162.1(2).

the iodine atom, I–N (2.101 Å), I–O (2.34 Å), and I–C (2.106 Å), all are within the range of typical single covalent bonds in organic derivatives of polyvalent iodine and are in good agreement with previously reported structures of chlorobenziodazoles.⁶ The solvated molecule of acetic acid is involved in a pair of synergetic hydrogen bonds with distances 1.751 Å (O1···HO5) and 2.091 Å (O4···HN). The covalent bonds with proton in this pair are H–O5 = 0.84 Å and H–N = 0.88 Å. To further clarify the structure of **4** in the desolvated state and to get insight into its reactivity, we investigated its reactions with azidotrimethylsilane, amides, and alcohols (Scheme 1).

Acetoxybenziodazole **4** reacts at room temperature with azidotrimethylsilane to afford a novel azide **5** in the form of a yellow, microcrystalline precipitate. Product **5** was identified by elemental analysis and IR and ¹H NMR spectra.⁸ Spectroscopic data on azide **5** are in good agreement with the previously reported data on azidobenziodoxoles.⁹ In particular, the IR spectrum of **5** displays a very intense peak of the azido function at 2034–2053 cm⁻¹, which is similar to the azido stretch in azidobenziodoxole⁹ at 2048 cm⁻¹. Azidobenziodazole **5** has a reactivity similar to that of azidobenziodoxoles⁹ and can be used as an efficient azidating reagent. Analogously to the unstable

(7) (a) Crystal data for **4** at 173 K with Mo K α radiation (Siemens SMART Platform CCD diffractometer): C₁₁H₁₂INO₅, FW = 365.12, *a* = 15.3268(2) Å, *b* = 4.7111(1) Å, *c* = 18.3258(1) Å, β = 107.152(1)°, monoclinic, *P*₂/c, *Z* = 4, *V* = 1264.38(3) Å³, *D*_c = 1.918 g·cm⁻³. *R* factor = 0.0430 for 1790 independent observed reflections (*I* > 2 σ (*I*)); weighted *R*² factor = 0.0943. (b) Crystal data for **7c** (173 K, Mo K α radiation, Siemens SMART Platform CCD diffractometer): C₁₁H₁₃F₃INO₅S, FW = 455.18, *a* = 7.8909(3) Å, *b* = 13.1034(4) Å, *c* = 15.8931(5) Å, β = 103.157(1)°, monoclinic, *P*₂/n, *Z* = 4, *V* = 1600.17(9) Å³, *D*_c = 1.889 g·cm⁻³. *R* factor = 0.0219 for 2521 independent observed reflections (*I* > 2 σ (*I*)); weighted *R*² factor = 0.0517. Further details on crystal structures of **4** and **7c** are available in the Supporting information.

(8) Preparation of **5**: To the mixture of acetate **4** (0.305 g, 1 mmol) in 10 mL of dry acetonitrile was added trimethylsilylazide (0.270 mL, 2 mmol) at room temperature under nitrogen with stirring. The mixture was stirred for additional 20 h at room temperature. The resulting pale yellow precipitate was filtered off and dried in vacuum to give 0.170 g (61%) of azide **5**; mp 122 °C (dec, expl.). IR (KBr): 3200 (br, NH), 3083, 3065 (Ar), 2053, 2034 (N₃), 1613 (C=O) cm⁻¹; ¹H NMR (DMSO-*d*₆): δ 8.5 (br, s, 1H, NH), 8.15 (d, 1H, *J* = 8 Hz), 7.98 (m, 2H), 7.79 (dd, 1H, *J* = 8 Hz). Anal. Calcd for C₇H₅IN₃O: C, 29.19; H, 1.75; N, 19.45. Found: C, 29.28; H, 1.72; N, 19.35. CAUTION: Azidobenziodazole **5** decomposes with an explosion upon heating to 122 °C and should be handled with care.

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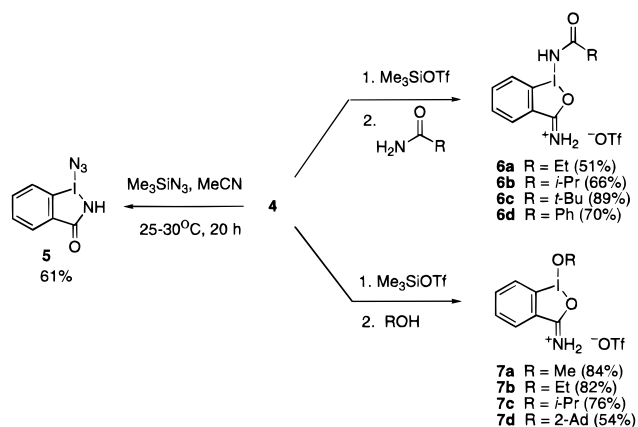
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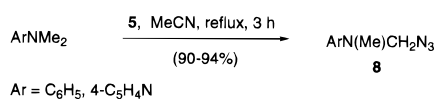
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Scheme 1



Scheme 2



azidoiodinanes,¹⁰ compound **5** reacts with dimethylanilines under mild conditions to afford the respective azidomethylene derivatives **8** (Scheme 2).

Amides and alcohols reacted with acetate **4** at room temperature after activation with trimethylsilyl triflate to afford rearranged products **6** and **7** (Scheme 1).¹¹ The structure of the iminium salt **7c** was unambiguously established by a single-crystal X-ray analysis (Figure 2),^{7b} and other products **6** and **7** were identified by elemental analysis and IR and ¹H NMR spectra. Specifically, ¹H NMR of amides **6** showed the signal of the amido group, NH, at $\delta = 7.7$ ppm and two different signals of the iminium protons, H_2N^+ , at about 8.3 and 8.4 ppm. In ¹H NMR of the alkoxy derivatives **7**, the signals of the iminium protons were observed at about 8.6 and 8.5 ppm.

A plausible mechanism of this rearrangement is shown in Scheme 3. The mechanism most likely includes ring opening

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(11) Preparation of **7c**: To the mixture of acetate **4** (0.305 g, 1 mmol) in 10 mL of dry acetonitrile was added trimethylsilyl triflate (0.195 mL, 1 mmol) under nitrogen and with stirring at room temperature. After the clear yellow solution was obtained, the solvent was evaporated, and the resulting yellow oil was dried in vacuum for 1–2 h at 40 °C. Then this residue was redissolved in 5–10 mL of dry acetonitrile and 1.5 mL of anhydrous isopropyl alcohol was added. The solution was stirred for an additional 1 h, then the solvent was evaporated to give white crystals, which were recrystallized from acetonitrile and ether. The white microcrystalline precipitate of **7c** was filtered off, washed with 2 × 10 mL of ether, and dried in vacuum. Yield: 0.344 g (76%); mp 151–152 °C (from CH_3CN). IR (KBr): 3360–3150 (br, NH), 3095 (Ar), 2972, 2931 (*i*-Pr), 1673 (C=N), 1275, 1265, 1165, 1020 (OTf) cm^{-1} . ¹H NMR (CD_3CN): δ 8.6 and 8.5 (2br. s, NH), 8.44 (d, 1H, $J = 8$ Hz), 8.23 (dd, 1H, $J = 8$ Hz), 8.10 (d, 1H, $J = 8$ Hz), 8.0 (dd, 1H, $J = 8$ Hz), 4.52 (septet, 1H, CH), 1.5 (d, 6H, Me). ¹⁹F NMR (CD_3CN): δ -78.90 (OTf). ¹³C NMR (CD_3CN): δ 172.6 (C=N), 137.7, 132.4, 131.1, 127.4, 126.3, 121.0 (all Ar), 121.5 (q, $J = 318$ Hz, OTf), 64.4 (CH), 25.1 (Me). Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{F}_3\text{INO}_5\text{S}$: C, 29.03; H, 2.88; N, 3.08. Found: C, 28.97; H, 2.84; N, 3.04. X-ray quality single crystals were obtained by slowly evaporating a solution of **7c** in CH_3CN in an open air container.

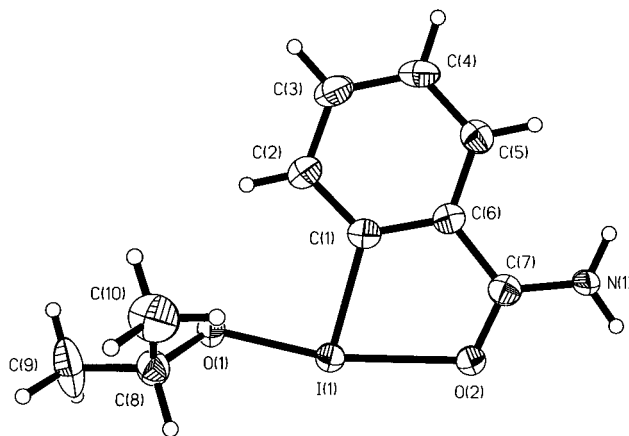
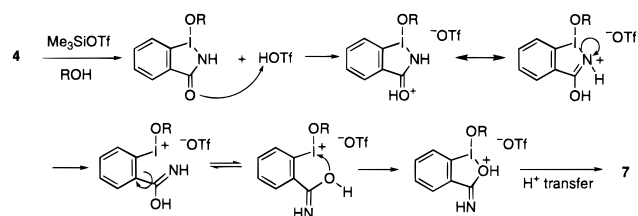


Figure 2. X-ray structure of **7c**. Selected bond lengths (Å): I(1)–C(1), 2.107(3); I(1)–O(1), 1.986(2); I(1)–O(2), 2.271(2); I(1)–O(5), 2.999; O(2)–C(7), 1.276(4); N(1)–C(7), 1.329(4). Selected bond angles (deg): O(1)–I(1)–C(1), 91.86(10); C(1)–I(1)–O(2), 76.28(9); O(1)–I(1)–O(2), 167.88(8).

Scheme 3



and ring closure in the protonated benzodioxole. We believe that the driving force for this novel rearrangement is the greater stability of the protonated imines **6** and **7** compared to that of the alternative protonated species.

In summary, the X-ray crystal structure of acetoxybenzodioxole **4**, different from the previously adopted structure, was reported. In retrospect, the modest catalytic activity of **4** in the cleavage of phosphates³ can be ascribed to **2** (X = OH, R = H), formed from **4** in aqueous base. Reaction of acetoxybenzodioxole **4** with azidotrimethylsilane produced azidobenzodioxazole **5**, which was found to be a useful azidating reagent toward dimethylanilines. A novel acid-catalyzed rearrangement of benzodioxoles to 3-iminobenzodioxoles was found in the reaction of acetoxybenzodioxole with amides and alcohols in the presence of trimethylsilyl triflate.

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Supporting Information Available: Selected experimental and characterization data and X-ray crystallographic report for compounds **4** and **7c** (29 pages). See any current masthead page for ordering and Internet access instructions.

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