

Preparation, Structure, and Unexpected Chemistry of Phosphoranyl-Derived Benziodoxoles

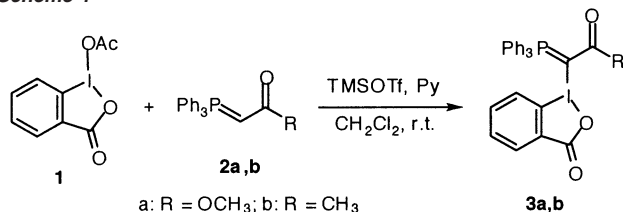
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In the past decade, there has been considerable interest and research activity focused on the chemistry of five-membered iodine(III) heterocycles, derivatives of benziodoxole.¹ The most important and best investigated heterocyclic iodane is 1-hydroxy-1,2-benziodoxol-3(1*H*)-one, the cyclic tautomer of 2-iodosylbenzoic acid. Other iodine-substituted benziodoxoles, such as peroxide,^{2a} azide,^{2b} cyanide,^{2b} amides,^{2b} and tosylate,^{2b,c} can be prepared by ligand exchange on iodine upon treatment of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one with the appropriate nucleophile. These various benziodoxole derivatives have found practical application as the reagents for oxidative functionalization of organic substrates.^{1,2}

In this communication, we report the preparation, solid-state structure, and an unexpected ligand exchange reaction of novel phosphoranyl-derived benziodoxoles **3**. Compounds **3** were prepared by the reaction of phosphoranes **2** with acetoxybenziodoxole **1** in the presence of trimethylsilyl triflate and pyridine (Scheme 1) and isolated in the form of stable, white, microcrystalline solids.³

Scheme 1



Products **3** were characterized by elemental analysis, spectroscopic data,³ and single-crystal X-ray analysis.⁴ X-ray crystallographic analysis of **3a** (Figure 1) shows that the benziodoxole ring system is essentially planar, deviating less than 0.12 Å from a least squares generated plane that also includes C(8) and O(3'). The C(7)–O(2) and C(7)–O(1) bond lengths at 1.227(4) and 1.256(5) Å, respectively, reflect the significant I–O(1) interaction, which is similar to that observed for the reported structures of benziodoxole derivatives, **4** and **5** (Table 1). The I–C(8) bond length is 2.056(3) Å, a value comparable to that of the analogous bond in derivatives **4**–**6**.⁵ The C(8)–P bond length for **3a** is close to that observed for the known noncyclic mixed phosphorus/iodonium ylide, tetrafluoroborate salt **6**.⁶ The solid-state packing of **3a** demonstrates the significance of secondary bonding interactions, which link individual molecules of **3a** into infinite chains via interactions between a carbonyl oxygen of one molecule with

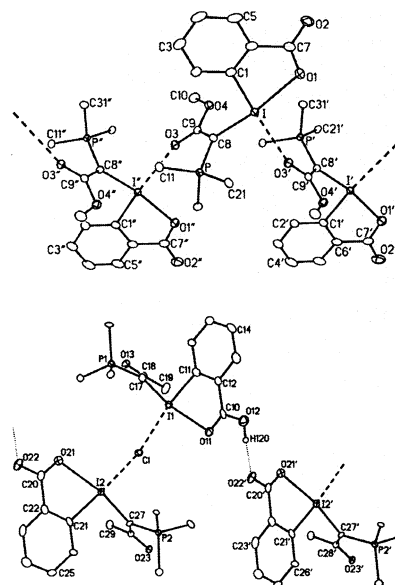


Figure 1. Secondary bonding within the crystal lattice of **3a** (top) and **3b** (bottom). Nonbonded interactions and H-bonded interactions are indicated with dashed and dotted lines, respectively. For clarity, only *ipso*-carbons of the phosphine phenyl rings are shown.

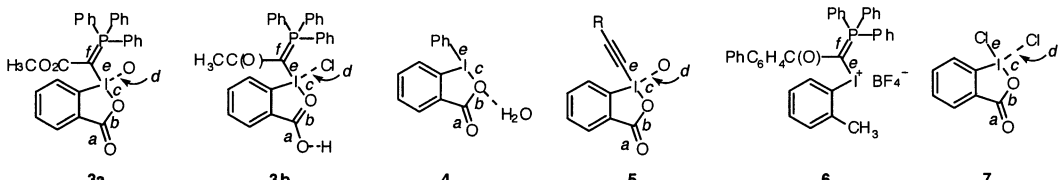
the I(III) center of its neighbor. This secondary bonding also affords an approximately square planar configuration about iodine, with a rather long I–O(3) bond length of 3.270(2) Å.

X-ray crystallographic analysis for **3b** shows two unique molecules in the unit cell (Figure 1), as well as a molecule each of CH₃CN and HCl.⁷ As for compound **3a**, the iodonium center of both molecules is best described as square planar, the result of the stereospecific coordination of both I(III) centers to the chlorine atom in a position trans to the aryl ligand. The I(1)–Cl and I(2)–Cl bond lengths are virtually identical, at 3.097(3) and 3.096(3) Å. These values are similar to those found for diphenyl iodonium chloride (Ph₂ICl), which exists as a chlorine bridged dimer, with I–Cl coordination distances of 3.064(3) and 3.105(3) Å.⁸ The I–Cl–I bond angle for **3b**, at 113.13(10)°, is substantially greater than that for Ph₂ICl at 86.52(7)°. Whereas no other examples of iodonium hydrochloride salts have been reported, Koser et al. have described the crystallographic analysis of the Bu₄NCl salt **7**.⁹ Despite the dissimilar structures of **3b** and **7**, the secondary bonding I–Cl interatomic distances are comparable. The more covalent I–Cl bond length of **7**, at 2.454(1) Å, is analogous to the covalent I–Cl bonds in PhICl₂ which are 2.45 Å.¹⁰ A considerable disparity exists in the exocyclic and endocyclic C–O bond lengths for the iodoxole ring of both molecules of **3b** in the crystal structure: C(10)–O(12) is appreciably longer than C(10)–O(11) (by 0.087 Å). This

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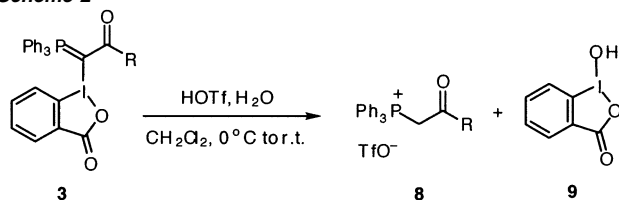
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Table 1. Selected Bonding Distances in Iodine(III) Compounds 3–7


compound	bond a (Å)	bond b (Å)	bond c (Å)	bond d (Å)	bond e (Å)	bond f (Å)
3a	1.227(4)	1.256(5)	2.484(2)	3.270(2)	2.056(3)	1.736(3)
3b (molecule 1)	1.313(15)	1.226(14)	2.605(8)	3.097(3)	2.061(12)	1.744(11)
3b (molecule 2)	1.276(13)	1.221(13)	2.569(8)	3.096(3)	2.060(10)	1.756(11)
4 (ref 5a)	1.223(4)	1.272(4)	2.478(4)		2.105(4)	
5 (ref 5b)	1.24(2)	1.28(2)	2.34(1)	2.77(1)	2.03(2)	
6 (ref 6a)					2.053(13)	1.710(13)
7 (ref 9)	1.220(5)	1.321(5)	2.145(3)	2.943(1)	2.454(1)	

difference is smaller for the other molecule, but still significant. The interatomic distance between O(22')–O(12) (2.491 Å) is consistent with intermolecular hydrogen bonding of a carboxylate with a carbonyl of the neighboring molecule. Although the position of the hydrogen was not detected in the diffraction analysis, the long C(10)–O(12) bond length supports the presence of the carboxylate as depicted (Figure 1). It should be noted that in comparison to molecules **3a**, **4**, and **5**, molecule **3b** displays an inverse relationship between the exocyclic and endocyclic I–O bond lengths, that is, a longer I–O bond within the iodoxole ring of **3b**. This is expected due to a reduced basicity of this oxygen resulting from coordination of the other oxygen to hydrogen. Overall, the solid-state arrangement of **3b** is ordered into infinite zigzagging chains via a combination of hydrogen bonding and secondary bonding interactions.

Preliminary experiments have demonstrated that the chemical properties of compounds **3** are quite different from those of the noncyclic phosphoranyl derivatives **6** and other known iodonium salts. In contrast to the noncyclic derivatives **6**,^{6b} benziodoxoles **3** are not reactive toward soft nucleophiles, such as PhS[−] and I[−] anions, even at elevated temperature (up to 100 °C) and in the presence of copper or palladium catalysts. On the other hand, compounds **3** readily react with strong acids (e.g., HOTf), affording phosphonium salts **8** and benziodoxole **9** as major products (Scheme 2). Phosphonium salts **8** were isolated from the reaction mixture in 60–85% yield and identified by elemental analysis and by comparison of NMR spectra with the literature data.¹¹

Scheme 2

This reaction represents an unusual example of a ligand exchange on an iodine(III) center resulting in the substitution of a carbon ligand with an oxygen ligand. This remarkable substitution is most likely explained by a stabilizing effect of the phosphonium moiety on the carbon leaving group in the protonated molecule of **3**.

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Supporting Information Available: Synthetic and characterization data for all new compounds (PDF) and X-ray crystallographic details for compounds **3a** and **3b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (3) **3b**: white crystals, isolated yield 43% (after recrystallization from CH₂Cl₂/ether); mp 175–176 °C. ¹H NMR (CDCl₃): δ 8.38 (d, 1H, *J* = 8 Hz), 7.8 (d, 1H, *J* = 8 Hz), 7.8–7.4 (m, 17H), 2.47 (s, 3H). ¹³C NMR (CDCl₃): δ 194.6, 166.9, 134.1, 133.4, 133.2, 132.6, 132.5, 130.2, 129.4, 124.7 (d, *J* = 92.7 Hz, CP), 122.5, 117.4, 44.4 (d, *J* = 91.8 Hz, C=P), 27.8. Anal. Calcd for C₂₈H₂₂O₃P·H₂O: C, 57.75; H, 4.15; I, 21.79. Found: C, 57.81; H, 3.94; I, 22.05. ES MS: *m/z* (%) 565 (100), [M + H]⁺, 317 (83), [M – IC₆H₄CO₂]⁺. Additional synthetic and characterization details are provided as Supporting Information.
- (4) Crystallographic Data. Compound **3a** (C₂₈H₂₂O₃P; formula weight 580.33) crystallized in the monoclinic space group *I2/a* (an alternate setting of *C2/c* [No. 15]) with *a* = 24.6924(19) Å, *b* = 9.6945(7) Å, *c* = 20.2514(16) Å; β = 101.6756(15)°, *V* = 4747.5(6) Å³, *Z* = 8, ρ = 1.624 g cm^{−3}, μ = 1.450 mm^{−1}, *T* = −80 °C; *R* = 0.0333 (3944 reflections with *F*_o² ≥ 2σ(*F*_o²)), *R*_w = 0.0812 for 4794 unique reflections with *F*_o² ≥ 3σ(*F*_o²). **3b**·CH₃CN (C₃₈H₄₈ClI₂NO₆P₂; formula weight 1206.16) crystallized in the monoclinic space group *P2₁/c* (No. 14) with *a* = 10.2285(9) Å, *b* = 29.139(3) Å, *c* = 17.8515(17) Å; β = 101.895(2)°, *V* = 5206.4(8) Å³, *Z* = 4, ρ = 1.539 g cm^{−3}, μ = 1.373 mm^{−1}, *T* = −80 °C; *R* = 0.0826 (4600 reflections with *F*_o² ≥ 2σ(*F*_o²)), *R*_w = 0.1865 for 10 670 unique reflections with *F*_o² ≥ 3σ(*F*_o²).
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