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ortho-Phosphoryl stabilized hypervalent iodosyl- and iodyl-benzene reagents

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Abstract—The synthesis and reactivity of a new IBX analogue (2-iodylphenyl)diphenyl-phosphine oxide 10 is described herein along with its analysis by single crystal X-ray diffraction. © 2005 Elsevier Ltd. All rights reserved.

1. Introduction

Hypervalent iodine compounds¹ continue to find importance as oxo- and nitrene-sources for metal catalyzed aziridinations² and epoxidations, respectively.³ The principal reagents used for these important transformations, iodosylbenzene (PhI=O) and (tosyliminoiodo)benzene (PhI=NTs), however, are dominated by strong intermolecular secondary bonding interactions, which render these compounds virtually insoluble in all non-reactive media.⁴ This fact inhibits the ability to enhance catalytic activity, perform careful mechanistic studies, grow crystals for single crystal X-ray diffraction studies, and to spectroscopically observe intermediates in oxidative processes.

Previously, we have found success by the incorporation of *ortho-tert*-butylsulfonyl groups into these two parent reagents that introduce intramolecular secondary bonding. The strategic location of a suitable negatively charged donor atom offers the electrophilic iodine center the opportunity to coordinate to a proximally located intramolecular oxygen atom rather than to a negatively charged donor atom of another molecule that might result in coordination polymerization. Some examples from our group (1–3) are shown in Chart 1.⁵ Whereas iodosylbenzene is practically insoluble in chloroform, a 0.08 M solution of **1a** can be prepared. Similarly, the





poor solubility of (tosyliminoiodo)benzene is enhanced 50-fold in CHCl₃ with the introduction of an *orthotert*-butylsulfonyl group in **1b**. Such reagents have been used successfully for *homogeneous* metal-catalyzed aziridinations and epoxidations.

More recently, this approach of integrating donor groups into hypervalent iodine compounds has led to the successful development of practical replacements for the synthetically useful oxidant IBX (1-hydroxy-1,2-benziodoxol-3(1*H*)-one-1-oxide), namely the IBX-amides **4**,⁶ IBX-esters **5**,⁷ and IBX-sulfonamides and sulfonate esters **6** (E = NH or O).⁸ Like 1–3, these reagents exhibit improved solubility compared to their

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simpler unsubstituted analogues. Polymer supported IBX-analogues have also been reported.⁹

The importance of secondary bonding interactions with regard to polycoordinated iodine chemistry has also been proven in developing chiral hypervalent iodine oxidants,¹⁰ for directing the self-assembly of amino acid derived benziodoxoles,¹¹ and for isolating novel complexes of diphenyl- λ^3 -iodanes with crown ethers.¹²

Given this recent excitement for these novel iodyl species as safe alternatives to IBX, we wish to report our work in which the *ortho-tert*-butylsulfonyl group of **1a** and **2** are replaced by the diphenylphosphoryl unit as a source of intramolecular secondary bonding. Herein, we report the preparation and characterization of a new potential IBX analogue (2-iodylphenyl)diphenylphosphine oxide, **10**.

2. Results and discussion

The requisite precursor to the title compounds, (2-iodophenyl)diphenylphosphine oxide, **8**, has been prepared by *ortho*-directed lithiation of Ph₃P=O followed by reaction with elemental iodine.¹³ The maintenance of low temperatures ($-25 \,^{\circ}$ C) over an extended period of time (72 h) during the lithiation step, however, made the two step process shown in Scheme 1 more attractive. (2-Bromophenyl)diphenylphosphine **7** was first prepared by using the method of Tunney and Stille¹⁴ (62%), and then converted to **8** by metal–halogen exchange and subsequent reaction with iodine (71%).

Oxidation of 8 to a fully characterized iodosylbenzene 9 that could be compared to iodosylbenzene 1a proved to be a challenging task. Subjecting 8 to the conventional protocol for the preparation of iodosylarenes, namely,



Scheme 1. Synthesis of 9 and 10.

treatment with peracetic acid followed by aqueous NaOH,¹⁵ yielded a mixture of unreacted 8 and triphenylphosphine oxide. An alternative method involving initial reaction of 8 with chlorine gas to generate ArICl₂ $(Ar = 2-Ph_2P(O)C_6H_4)$, followed by hydrolysis with base,¹⁶ was unsuccessful due to failure to obtain the ArICl₂ intermediate. It was found, however, that if the material produced from the action of peracetic acid on 8 was dissolved in CHCl₃ and washed with cold H₂O until the odor of acetic acid was eliminated, evaporation of the chloroform followed by trituration with ether would give a product consistent with 9.17 Elemental analysis of this white solid from two different preparations matched the expected composition along with a fractional amount of CHCl₃ (0.86). ¹H NMR analysis indicated a downfield shift of the signal for the proton *ortho* to the iodine atom from δ 8.01 in **8** to δ 8.78 in 9, consistent with what is observed for other hypervalent iodine compounds. Analysis by ³¹P NMR spectroscopy gave a correspondingly downfield shift from δ 33.7 in 8 to δ 38.4 in 9.

Attempts to crystallize the putative iodosylbenzene **9** from a mixture of chloroform and benzene yielded X-ray diffraction quality single crystals. Analysis of the data, however, revealed the identity of the material as the iodyl derivative $10.2H_2O$ (Fig. 1). As the precursor iodobenzene **8** was highly crystalline, an X-ray diffraction was also performed on this substance to allow comparisons to **10** (Fig. 2).

Several structural features of **10** merit comment, in particular, the features that differ from those found in the



Figure 1. X-ray crystal structure of iodylarene 10. Selected distances [Å] and angles [°]: I1–O3 1.789(12), I1–O2 1.818(10), I1–O1 2.603(11), I1–C1 2.153(15), P1–O1 1.498(11), P(1)–C(1) 1.808(16), I1···O2' 2.564; C1–I1–O3 94.1(6), O3–I1–O2 103.7(6), C1–I1–O2 93.2(6), O(1)–I(1)–O(3) 167.9(5).



Figure 2. Single crystal X-ray structure of **8**. Selected distances [Å] and angles [°]: I1–C1 2.115(6), P1–O1 1.474(4), P1–C2 1.811(5); O1–P1–C2 114.7(7).

structural analyses of 2 and 8. First, as anticipated, there is a close contact of the phosphoryl oxygen atom with the iodine atom. This I...O3 distance of 2.612 Å is comparable to the value of 2.693(2) Å found in sulfone derivative 2, and significantly shorter than the $I \cdots O3$ distance of 3.291 Å determined for 8. Intramolecular secondary bonding in 10 induces a roughly coplanar geometry for atoms O3, P1, C2, C1, and I1 (mean deviation from best plane 0.12 Å). However, careful analysis of this five atom array reveals that both the I1 and O3 atoms are slightly displaced from either side of the best plane of the six aromatic carbons of the iodobenzene ring by -0.29 and +0.27 Å, respectively. Compound 2 shows displacements of the I and O3 atoms from the same side of the least squares plane of the six aromatic carbons of the iodobenzene ring by +0.39 and +0.50 Å, respectively. Such minor displacements are possibly induced by the close C6-H···O1 contacts of 2.38 and 2.39 Å that occur in 10 and 2. The I-O1 and I-O2 bond lengths for 10 are nearly identical to those determined for 2, as are the bond angles involving the iodyl unit. One of the two water molecules (O4) within the lattice of 10 appears to engage in some degree of hydrogen bonding to O1 of the iodyl unit (hydrogen atoms of O4 located and refined) with a $O1 \cdots H(O4)$ distance of 2.25 Å. By contrast, O1 for 2 is found to participate in hydrogen bonding to a dichloromethane molecule found in the crystal (O1···H distance of 2.55 Å). The hydrogen atoms of the second molecule of water in 10 were not located with confidence, leaving open the possibility of other hydrogen bonding interactions.

Molecules of **10** are aggregated in the solid state to form dimers held together by intermolecular $I \cdots O2$ secondary bonds (2.57 Å), comparable in length to the shorter of the two intermolecular $I \cdots O2$ secondary bonds found in **2**. The presence of these two $I \cdots O$ secondary bonds in 2 leads to an infinite bifurcated polymeric structure. While one can consider 10 to be dimeric in the solid state, as we have chosen to show in Figure 2, close contacts of the iodine atoms with neighboring iodobenzene ring (but not with the same molecule depicted in Fig. 2) indicate that there are most likely significant I...arene interactions as well. This interaction is trans to O2 and the I1–O1 vector is parallel to this aromatic ring placing the iodine center at a distance of 3.47 Å above this neighboring plane of carbon atoms. The iodine atom is not located above the centroid of this ring, and is nearly above C5 of this ring (3.57 Å). This geometry places O1 3.76 Å above C3 of the same ring. The crystal structure of MesINTs (Mes = $2,4,6-Me_3C_6H_2$) revealed a similar I...arene interaction with a I...centroid distance of 3.46 Å.¹⁸ In summary, the packing diagram of 10 is complex, and the presence of intermolecular $I \cdots O$ secondary bonds, $I \cdots$ arene interactions, and hydrogen bonding makes for a tightly held network polymer.

The genesis of **10** from efforts to crystallize **9** is most likely the result of a disproportionation reaction. It is well known that iodosylbenzenes can undergo disproportionation¹⁹ to give an equivalent of the reduced iodobenzene and an equivalent of iodylbenzene. This tendency has been suggested to be more prominent in substituted compounds.²⁰

A more direct path to the highly stable iodylbenzene **10** was realized by treatment of **8** with aqueous sodium hypochlorite under phase transfer²¹ conditions (71%).²² Compound **10** is insoluble in chloroform, acetonitrile, benzene, and ether.

Preliminary investigations into the oxidation behavior of **9** and **10** have found them to be active oxidants. Triphenylphosphine is rapidly and quantitatively converted at room temperature to triphenylphosphine oxide in *d*-chloroform in the presence of **9** or **10**. Similarly, methyl *p*-tolyl sulfide is converted to the corresponding sulfoxide in moderate yields (41% and 30%, respectively) after protracted (2 days) exposure to **9** or **10** in *d*-chloroform at room temperature. Thus, the present materials appear to be less effective than the IBX-ester analogue **5** (R = *i*-Pr) for selective oxidations.^{7b} An exploration of further oxidation chemistry of these compounds is currently underway.

Acknowledgments

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Supplementary data

Cystallographic data for the structural analyses of **8** and **10** have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 271725 and 271726). Copies of this information can be obtained free of charge via www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.05.111.

References and notes

- For some reviews see: (a) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* 2002, 102, 2523–2584; (b) Koser, G. F. *Aldrichim. Acta* 2001, 34, 89–102; (c) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* 1996, 96, 1123–1178; (d) Koser, G. F. In *The Chemistry of Halides, Psuedohalides* and Azides, Supplement D2; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1995, pp 1173–1274; (e) Varvoglis, A. *The Chemistry of Polycoordinated Iodine*; VCH: New York, 1992; (f) *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis*; Wirth, T., Ed.; Topics in Current Chemistry; Springer: Berlin, 2003; Vol. 224.
- For some examples of nitrene transfer see: (a) Dauban, P.; Dodd, R. H. Synlett 2003, 1571; (b) Osborn, H. M.; Sweeney, J. Tetrahedron: Asymmetry 1997, 8, 1693–1715; (c) Johannsen, M.; Jørgensen, K. A. Chem. Rev. 1998, 98, 1689–1708; (d) Lautens, M.; Klute, W.; Tam, W. Chem. Rev. 1996, 96, 49–92; (e) Li, Z.; Quan, R. W.; Jacobsen, E. N. J. Am. Chem. Soc. 1995, 117, 5889–5890; (f) Li, Z.; Conser, K. R.; Jacobsen, E. N. J. Am. Chem. Soc. 1993, 115, 5326–5327; (g) Evans, D. A.; Bilodeau, M. T.; Faul, M. M. J. Am. Chem. Soc. 1994, 116, 2742–2753; (h) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. J. Org. Chem. 1991, 56, 6744–6746.
- For some examples of oxo-transfer see: (a) Palucki, M.; Pospisil, P. J.; Zhang, W.; Jacobsen, E. N. J. Am. Chem. Soc. 1994, 116, 9333–9334; (b) Holm, R. H.; Donahue, J. P. Polyhedron 1993, 12, 571–589; (c) Collman, J. P.; Zhang, X.; Lee, V. J.; Uffelman, E. S.; Brauman, J. I. Science 1993, 261, 1404–1411; (d) Ostovic, D.; Bruice, T. C. Acc. Chem. Res. 1992, 25, 314–320; (e) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. J. Am. Chem. Soc. 1990, 112, 2801–2803.
- Batchelor, R. J.; Birchall, T.; Sawyer, J. F. Inorg. Chem. 1986, 25, 1415–1420.
- (a) Meprathu, B. V.; Protasiewicz, J. D. ARKIVOC 2003, 83–90;
 (b) Macikenas, D.; Skrzypczak-Jankun, E.; Protasiewicz, J. D. Angew. Chem., Int. Ed. 2000, 39, 2007– 2010;
 (c) Macikenas, D.; Skrzypczak-Jankun, E.; Protasiewicz, J. D. J. Am. Chem. Soc. 1999, 121, 7164–7165.
- (a) Zhdankin, V. V.; Koposov, A. Y.; Netzel, B. C.; Yashin, N. V.; Rempel, B. P.; Ferguson, M. J.; Tykwinski, R. R. Angew. Chem., Int. Ed. 2003, 42, 2194–2196; (b) Zhdankin, V. V. Curr. Org. Synth. 2005, 2, 121–145.
- (a) Zhdankin, V. V.; Litvinov, D. N.; Koposov, A. Y.; Luu, T.; Ferguson, M. J.; McDonald, R.; Tykwinski, R. R. J. Chem. Soc., Chem. Commun. 2004, 106–107; (b) Koposov, A. Y.; Zhdankin, V. V. Synthesis 2005, 22.
- (a) Koposov, A. Y.; Litvinov, D. N.; Zhdankin, V. V. *Tetrahedron Lett.* **2004**, *45*, 2719–2721; (b) Zhdankin, V.; Goncharenko, R. N.; Litvinov, D. N.; Koposov, A. Y. *ARKIVOC* **2005**, 8–18.

- Chung, W.-J.; Kim, D.-K.; Lee, Y.-S. *Tetrahedron Lett.* 2003, 44, 9251–9254.
- (a) Hirt, U. H.; Spingler, B.; Wirth, T. J. Org. Chem. 1998, 63, 7674–7679; (b) Wirth, T.; Hirt, U. H. Tetrahedron: Asymmetry 1997, 8, 23–26; (c) Hirt, U. H.; Schuster, M. F. H.; French, A. N.; Wiest, O. G.; Wirth, T. Eur. J. Org. Chem. 2001, 8, 1569–1579.
- 11. Zhdankin, V. V.; Koposov, A. Y.; Smart, J. T. J. Am. Chem. Soc. 2001, 123, 4095–4096.
- (a) Ochiai, M.; Suefuji, T.; Miyamoto, K.; Tada, N.; Goto, S.; Shiro, M.; Sakamoto, S.; Yamaguchi, K. J. Am. Chem. Soc. 2003, 125, 769–773; (b) Ochiai, M.; Miyamoto, K.; Shiro, M.; Ozawa, T.; Yamaguchi, K. J. Am. Chem. Soc. 2003, 125, 13006–13007; (c) Ochiai, M.; Suefuji, T.; Miyamoto, K.; Shiro, M. J. Chem. Soc., Chem. Commun. 2003, 1438–1439.
- 13. Desponds, O.; Schlosser, M. J. Organomet. Chem. 1996, 507, 257–261.
- 14. Tunney, S. E.; Stille, J. K. J. Org. Chem. 1987, 52, 748-752.
- 15. Saltzman, H.; Sharefkin, J. G. Org. Synth. 1963, 43, 60-61.
- Lucas, H. J.; Kennedy, E. R.; Formo, M. W. Org. Synth. 1955, Coll. Vol. 3, 483–485.
- 17. Compound 9: A solution of 8 (0.505 g, 1.30 mmol) and tetra-*n*-butylammonium bromide (25 mg) in CH₂Cl₂ (20 mL) was stirred vigorously with 50 mL of 5.25% aqueous sodium hypochlorite (Clorox[®]) for a period of 1 h and then allowed to stand overnight. Filtration of the resulting crystals in the organic layer gave 9 (0.403 g, 71%); mp 205 °C (exp. dec.); ¹H NMR (DMSO-*d*₆) 8.48 (dd, 1H), 7.96 (t, 1H), 7.54–7.82 (m, 14H); ¹³C NMR (DMSO-*d*₆) 138.9, 138.2, 137.3 (d, $J_{CP} = 10.3$ Hz), 137.2 (d, $J_{CP} = 42.8$ Hz), 136.4, 135.0, 134.2, 133.3 (d, $J_{CP} = 93.2$ Hz), 133.2 (d, $J_{CP} = 7.2$ Hz), 127.7 (d, $J_{CP} = 4.6$ Hz); ³¹P δ 39.5.
- Boucher, M. A.; Macikenas, D.; Ren, T.; Protasiewicz, J. D. J. Am. Chem. Soc. 1997, 119, 9366–9376.
- Nappa, M. J.; Tolman, C. A. Inorg. Chem. 1985, 24, 4711– 4719.
- 20. Bressan, M.; Morvillo, A. Inorg. Chem. 1989, 28, 950– 953.
- Bayraktaroglu, T. O.; Gooding, M. A.; Khatib, S. F.; Lee, H.; Kourouma, M.; Landolt, R. G. J. Org. Chem. 1993, 58, 1264–1265.
- 22. Compound **10**: A solution of peracetic acid (2 mL, 32% in dilute acetic acid) was added to **8** (0.602 g, 1.48 mmol) and stirred overnight at room temperature (a solution was obtained within 1 h). The solution was concentrated in vacuo to a moist, white solid. After trituration with water followed by ether, the solid was dissolved in chloroform (20 mL) and further washed with water (3 × 10 mL). Concentration of the organic phase afforded **10**; mp 105 °C; ¹H NMR (CDCl₃) δ 8.78 (d, *J* = 7.8 Hz, 1H), 7.94 (m, 1H), 7.4–7.9 (m, 12H); ¹³C NMR (DMSO-*d*₆) δ 154.5, 132.9, 132.6, 132.1, 131.8, 131.1, 131.0, 129.7, 129.0, 128.8, 122.5; ³¹P NMR (CDCl₃) δ 38.5; HRMS 403.9808, calcd 403.9827; Anal. Calcd for C₁₈H₁₄IO₂P·0.86CHCl₃: C, 43.32; H, 3.64. Found: C, 43.36; H, 3.31.