

A New Class of Iodonium Ylides Engineered as Soluble Primary Oxo and Nitrene Sources

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Transition metal catalyzed atom and group transfer reactions are important tools in both Nature's and the synthetic chemist's arsenal for the assembly of functionalized molecules. Iodosylbenzene (PhIO) has served as a critical primary oxygen atom source in many synthetic and biomimetic studies.¹ The emergence of (tosyliminoiodo)benzene² (PhINTs, Ts = *p*-toluenesulfonyl), a nitrene analogue of iodosylbenzene, has allowed parallel development of new classes of powerful catalytic imination and aziridination reactions.³ These two iodonium ylides are popular due to their effectiveness, relative ease of preparation, and rather innocuous byproduct PhI.⁴ Catalytic reactions that employ these reagents are heterogeneous due to their insoluble nature,⁵ and efforts to improve catalytic performance or to gain mechanistic insights are hindered. Systematic studies of the structures of PhIO and ArINSO₂Ar' reveal extensive networks of I···O and I···N secondary bonds and highly aggregated polymeric networks.^{6,7} We initially reasoned that disruption of these intermolecular electrostatic forces could be achieved by the addition of external materials having large dipoles, such as trimethylamine-*N*-oxide. Although PhINTs can be readily solubilized by Me₃NO in CDCl₃, a drop in the activity of PhINTs occurs.⁸ New iodonium ylides ArIX (X = O or NTs) having strong internal dipoles have thus been engineered for introducing intramolecular I···O secondary bonds to replace intermolecular I···N and I···O secondary bonds. These highly reactive primary oxo and tosylimino sources display impressive solubility in organic media. In addition, single-crystal X-ray analysis of the primary tosylimino source reveals several fascinating structural features.

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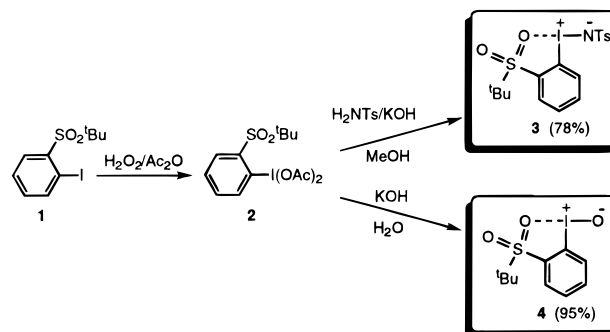
(5) PhIO and PhINTs solvolyze in methanol. See: (a) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563–1565. (b) White, R. E. *Inorg. Chem.* **1987**, *26*, 3916–3919.

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Scheme 1



The synthesis of the organoiodine(III) species is outlined in Scheme 1. Oxidation of **1**⁹ with peracetic acid leads to the (diacetoxyiodo)arene **2**. For maximal and most expedient yields of the target ylides, **2** is used without purification or workup. The corresponding pale yellow (tosyliminoiodo)arene (**3**) and bright yellow iodosylarene (**4**) are thus obtained in 78 and 95% yields (based on **1**), respectively.¹⁰ The solution properties of **3** and **4** are quite remarkable. Compound **3**, for example, will readily dissolve in chloroform (ca. 0.14 M at room temperature, at least a 50-fold increase over PhINTs), dichloromethane, and acetonitrile. The impressive solubility properties of **3** are exhibited, albeit to a lesser extent, in the corresponding iodosylarene **4**. Solutions of up to 0.08 M in **4** can be obtained in CHCl₃. Solutions of **3** in CDCl₃ show little signs of decomposition during a 20 h period (<8%), thereby demonstrating the remarkable ability of the internal I···O secondary bond to stabilize the low-coordinate hypervalent iodine atom. Such results are significant in that many reactions utilizing PhINTs are plagued by hydrolytic side reactions.¹¹ ¹³C{¹H} NMR spectra of **3** and **4** in CDCl₃ display resonances shifted downfield for the *ipso* aromatic carbon atoms at 115.5 and 117.9 ppm relative to **1** (δ 94.6) that clearly signal oxidation to I(III).¹²

Single crystals of **3** suitable for X-ray structural analysis have been grown from acetonitrile and the resulting details are presented in Figure 1.¹³ Several features are noteworthy. First, **3** is loosely associated into centrosymmetric dimers by long-range intermolecular I···N and I···O bonds (>3.0 Å), quite unlike the infinite polymeric chains adopted in the solid state for PhIO and PhINTs. Second, as anticipated, one of the sulfonyl oxygen atoms

(9) Compound **1** was prepared in two steps from Ph^tBu in 96% overall yield. See: (a) Ipatieff, V. N.; Pines, H.; Friedman, B. S. *J. Am. Chem. Soc.* **1938**, *60*, 2731–2734. (b) Iwao, M.; Iihama, T.; Mahalanabis, K. K.; Perrier, H.; Snieckus, V. *J. Org. Chem.* **1989**, *54*, 24–26. (c) Clayden, J.; Cooney, J. J. A.; Julia, M. J. *Chem. Soc., Perkin Trans. 1* **1995**, 7–14.

(10) Compound **3**: Mp 148–149 °C dec. ¹H NMR (CDCl₃, 200 MHz) δ 8.35 (d, *J* = 8.2 Hz, 1H), 7.78–7.93 (m, 4H), 7.66–7.75 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 2.39 (s, 3H), 1.45 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz) δ 142.1, 140.7, 136.2, 133.5, 132.1, 130.7, 129.4, 128.7, 126.8, 115.5, 63.6, 23.5, 21.4. Anal. Calcd for C₁₇H₂₀INO₄S: C, 41.38; H, 4.09; N, 2.84. Found: C, 41.10; H, 4.00; N, 2.69. Compound **4**: Mp 126 °C dec. ¹H NMR (CDCl₃, 300 MHz) δ 8.09 (m, 1H), 7.88 (m, 2H), 7.66 (m, 1H), 1.39 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz) δ 135.4, 132.7, 132.0, 129.7, 127.2, 117.9, 63.3, 23.5. Anal. Calcd for C₁₀H₁₃IO₃S: C, 35.31; H, 3.85. Found: C, 34.93; H, 4.10.

(11) This decreased sensitivity to water is analogous to the added stability imparted by intramolecular secondary Bi···N bonding in a bismuth tosylimide. See: Ikegami, T.; Suzuki, H. *Organometallics* **1998**, *17*, 1013–1017.

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(13) Crystal data for **3**, C₁₇H₂₀INO₄S: Monoclinic, *P*2₁/*n*, *a* = 11.252(2) Å, *b* = 10.092(2) Å, *c* = 17.430(4) Å, *b* = 99.40(3)°, *Z* = 4, ρ_{calc} = 1.678 g/cm³. 13338 reflections (5080 unique) collected at 293(1) K for a crystal of 0.16 × 0.08 × 0.06 mm³ using a Bruker SMART Platform with CCD 1K detector and Mo radiation with graphite monochromator, 2θ < 60°. Final refinement for 287 parameters converged to R1 = 0.0403 (3575 reflections with *I* > 2σ(*I*)), and wR2 = 0.0746 (all data).

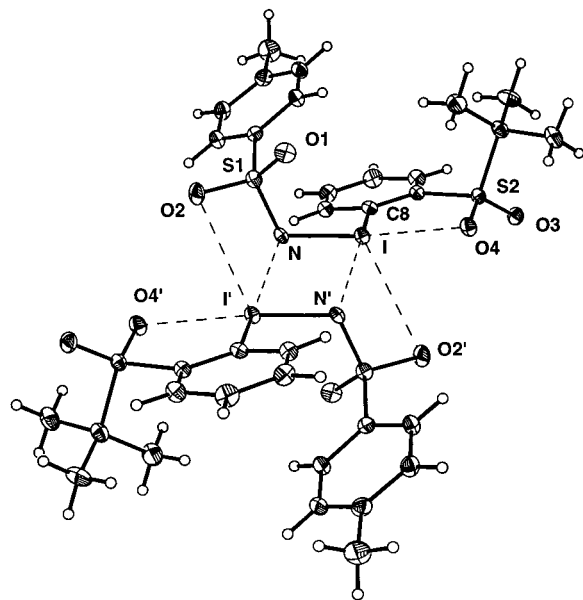
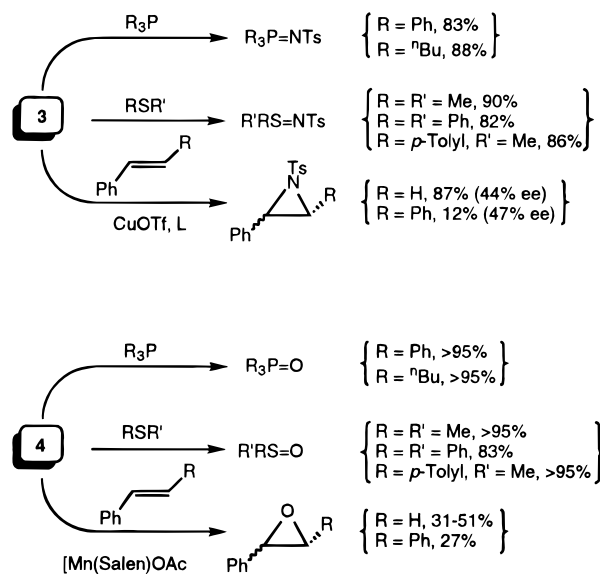


Figure 1. Structural diagram for compound **3**. Selected bond distances (Å) and angles (deg): I–N, 1.982(3); I–C8, 2.145(3); I···O4, 2.677(3); I···N', 3.105(3); I···O2', 3.550(3); S1–N, 1.629(3); S1–O1, 1.446(3); S1–O2, 1.440(3); S2–O3, 1.437(2); S2–O4, 1.455(2); N–I···O4, 170.92(9); C8–I···O4, 73.3(1); C8–I–N, 97.9(1).

forms a short intramolecular I···O secondary bond to the hypervalent iodine atom with a I···O bond length of 2.667(3) Å. Third, the nitrogen atom of the NTs group is located essentially in the plane of the iodoarene ring trans to the sulfonyl oxygen atom of the sulfone moiety (O2). The NSO₂Ar' group in all previous structurally characterized ArINSO₂Ar' is located above the plane of the iodoarene ring, presumably a result of steric interactions between the NSO₂Ar' group and the ortho proton of the iodoarene ring.⁷ The strength of the intramolecular I···O bond seems sufficient to overcome this interaction and thus **3** resembles a number of cyclic λ³-iodinanes.⁴

Initial assessment of the ability of **3** and **4** as primary sources of oxygen atoms and tosylimino groups is summarized in Scheme 2. Compound **3** and **4** react rapidly with tertiary phosphines and thioethers and afford the corresponding products of oxo and tosylimino transfer.¹⁴ Copper-catalyzed aziridination of styrene and *trans*-stilbene by **3** proceeds efficiently for both substrates.¹⁵ Iodosylarene **4** is also effective for the manganese-catalyzed epoxidations of styrene and stilbene.¹⁶ For example, the epoxidation of styrene by **4** catalyzed by [Mn(salen)OAc] produced the expected epoxide in 31% yield. This reaction, however, is also accompanied by a considerable amount of a precipitate that we have identified as the iodoxyarene **5**.¹⁷ The iodoxyarene results from a competitive disproportionation of the iodosylarene by the

Scheme 2



catalyst (eq 1).



Indeed, increasing the ratio of styrene to **4** to 20:1 from 5:1 increases the amount of epoxide formed (51%) and reduces the quantity of **5** formed. The manganese-catalyzed disproportionation of **4** is rapid (and quantitative) in the absence of olefin. In the absence of catalyst the disproportionation of **4** is slow ($t_{1/2} \sim 6$ h in CDCl₃). Disproportionation of iodosylbenzene has been previously noted and it has been predicted that an iodosylarene solubilized by introducing substituents would be increasingly susceptible to disproportionation unless steric effects could inhibit disproportionation.^{18,19}

The new soluble iodonium ylides presented here are expected to lend added flexibility to catalytic atom and group transfers by offering homogeneous conditions, to provide opportunities to conduct studies at reduced temperatures, and to facilitate the search of new catalysts for atom and group transfer reactions by combinatorial methods.²⁰ We are currently also exploring means for the incorporation of chiral dipole groups into these ylides.²¹

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Supporting Information Available: Experimental details and characterization of **1–4** and tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths, and angles for **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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 (17) Compound **5**: Mp 160–165 dec. ¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.46 (m, 1H), 8.13 (m, 1H), 7.96 (m, 1H), 7.87 (m, 1H), 1.32 (s, 9H). ¹³C{¹H} NMR (DMSO-*d*₆, 75.5 MHz) δ 23.2, 61.2, 124.0, 131.2, 132.0 (this signal splits into two signals in a DMSO-*d*₆/benzene-*d*₆ mixture), 135.0, 148.0.

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