Pergamon

Tetrahedron Letters 43 (2002) 5735–5737

TETRAHEDRON
LETTERS

Complexes of hypervalent iodine compounds with nitrogen ligands

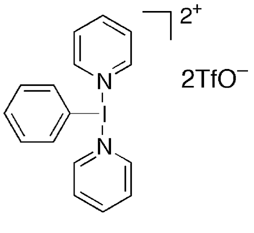
Viktor V. Zhdankin,* Alexey Y. Koposov and Nikolai V. Yashin

Department of Chemistry, University of Minnesota Duluth, Duluth, MN 55812, USA

Received 14 June 2002; revised 19 June 2002; accepted 20 June 2002

Abstract—The stable 1:1 complexes of benziodoxole with heterocyclic amines were prepared by a reaction of 1-hydroxy-1*H*-1λ^3-benzo[*d*][1,2]iodoxol-3-one with trimethylsilyl triflate and pyridine or 1,1′-sulfonyldiimidazole. The structure of these complexes was confirmed by spectroscopic data and a high resolution ES mass-spectrometry. A novel pentavalent iodine complex with a chelating, polydentate nitrogen ligand was prepared from bis(acetoxy)iodylbenzene, trimethylsilyl triflate, and 2,2′-bipyridyl.

During the last few years, hypervalent iodine compounds have received a widespread practical application in organic synthesis as versatile oxidizing reagents.[1] It has also been recognized that there are many similarities between hypervalent main group compounds and organic transition metal complexes.[1,2] In particular, the reactions of hypervalent iodine compounds are commonly discussed in terms of oxidative addition, ligand exchange, and reductive elimination that are typical of the transition metal chemistry.[1,2] It can be anticipated that these similarities can be further extended to the preparation of hypervalent iodine complexes with nitrogen ligands, which are commonly used in the transition metal chemistry. To the best of our knowledge, the only report in the literature example of hypervalent iodine complex with nitrogen ligands is represented by a relatively unstable complex of iodosylbenzene with pyridine, **1**, and similar complexes of iodosylbenzene with 4-(dimethylamino)pyridine, 1-methylimidazole, and quinoline.[3] It was recently demonstrated that pyridinium complex **1** can be used as a highly electrophilic and selective reagent for the preparation of the novel and potentially important phosphorane-derived phenyliodonium triflates.[4] Considering potential significance of such complexes for organic synthesis, we decided to investigate the complexation of important iodine(III) and iodine(V) compounds with the mono- and polydentate nitrogen ligands.



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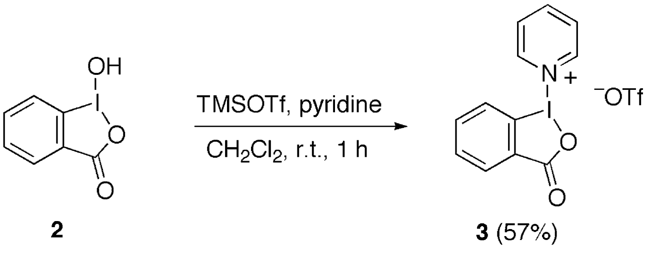
We have studied the reactions of various common nitrogen ligands with the derivatives of benziodoxole[5] and iodylbenzene[1] in the presence of trimethylsilyl triflate. Benziodoxole **2** reacted with trimethylsilyl triflate and then with pyridine in dichloromethane with the formation of a white, microcrystalline precipitate of complex **3** (Scheme 1), which was isolated by filtration as a stable monohydrate.[6a]

Pyridinium complex **3** was identified by NMR, IR, ES mass-spectrometry, and elemental analysis.[6] In particular, the proton NMR spectra of this compound showed



Scheme 1.

Keywords: hypervalent iodine; benziodoxole; iodylbenzene; iodine complexes; nitrogen ligands.

* Corresponding author. Tel.: (218) 726-6902; fax: (218) 726-7394; e-mail: vzhdanki@d.umn.edu

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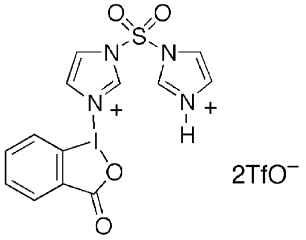
PII: S0040-4039(02)01192-9

signals of five pyridinium protons and four protons of the benziodoxole fragment, while the IR spectrum displayed a characteristic peak of the benziodoxole carbonyl at 1609 cm^{-1}, as well as the respective strong absorptions of the triflate anion in the area between 1300 and 1100 cm^{-1}. The structure of complex **3** was further supported by a high resolution ES mass-spectrum, in which the intense peaks of the molecular ion, $(M\text{–OTf})^+$, and of the benziodoxole fragment were present.

Similar 1:1 complexes were obtained in the reactions of benziodoxole **2** with 2,6-lutidine, piperidine, morpholine, and quinuclidine. The stability of these adducts, however, was lower as compared to the pyridinium complex **3**. Specifically, in the presence of moist air, complexes of benziodoxole with aliphatic amines underwent hydrolysis with the formation of benziodoxole **2** and the respective ammonium triflate salts.

It was especially interesting to investigate the complexation of benziodoxole **2** with polydentate nitrogen ligands, such as 2,2′-bipyridyl and 1,1′-sulfonyldiimidazole, which are commonly used in the transition metal chemistry. The reaction of benziodoxole **2** with 1,1′-sulfonyldiimidazole and two molar equivalents of trimethylsilyl triflate was carried out at room temperature in dichloromethane to afford a white, microcrystalline precipitate of complex **4**, which was isolated by filtration in 43% yield.[6b]



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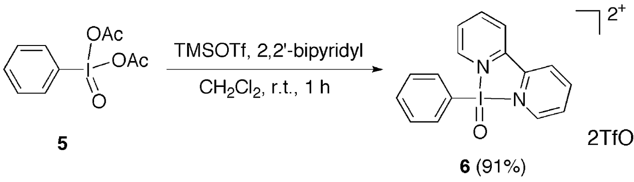
According to elemental analysis and spectroscopic data, only one of the nitrogen atoms of sulfonyldiimidazole is coordinated on the iodine center in complex **4**, while the second imidazolium ring is protonated with trifluoromethanesulfonic acid. Specifically, both IR and ^1H NMR spectra indicate the presence of the protonated imidazolium ring in the molecule of **4**. In the ES mass-spectrum, the peaks of the molecular ion, $(M\text{–OTf})^+$, and of the benziodoxole fragment are present. A similar complex with the monocoordinated/monoprotonated nitrogen ligand was formed in the reaction of benziodoxole **2** with 2,2′-bipyridyl. The formation of a hypothetical complex with both nitrogens of the ligand coordinated on the same iodine atom was not observed, probably due to the restrictive trigonal–bipyramidal geometry of trivalent iodine with the most electronegative ligands occupying the axial positions.[1]

It is known from the literature that the geometrical features of the pentavalent iodine are less restrictive compared to iodine(III), which allows the preparation of some cyclic derivatives with polydentate oxygen ligands.[7] These literature data encouraged us to study the reactions of pentavalent iodine derivatives with 2,2′-bipyridyl as a typical polydentate nitrogen ligand. At first, we attempted the preparation of complexes of iodylbenzene, $PhIO_2$, with 2,2′-bipyridyl in the presence of trimethylsilyl triflate at room temperature in dichloromethane. No reaction was observed under these conditions, probably due to the low solubility of $PhIO_2$ in organic solvents. In order to improve the solubility, iodylbenzene was converted to bis(acetoxy)iodylbenzene **5** by the treatment with acetic anhydride according to the known procedure.[8] Diacetate **5** was then treated with trimethylsilyl triflate to afford a stable, microcrystalline complex **6** (Scheme 2).[9]



Scheme 2.

Compound **6** was identified by IR, NMR, ES mass-spectrometry, and elemental analysis.[9] In particular, in the IR spectrum of this product the characteristic I=O absorption was present at 756 cm^{-1}. ^1H NMR spectrum showed the appropriate signals of the bipyridyl and the phenyl protons.[10] In the ES mass-spectrum, the peaks of the molecular ion, $(M\text{–OTf})^+$, and the respective fragments were present. A similar complex was formed in the reaction of bis(acetoxy)iodylbenzene with 1,1′-sulfonyldiimidazole and trimethylsilyl triflate. The stability of this adduct, however, was lower compared to complex **6**.

In conclusion, we have reported the preparation of the novel complexes of benziodoxole with aromatic amines and the first example of a pentavalent iodine complex with a chelating, polydentate nitrogen ligand. These complexes are potentially useful as mild electrophiles and selective oxidizing reagents.

Acknowledgements

This work was supported by a research grant from the National Science Foundation (NSF/CHE-0101021).

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6. **Representative experimental data**

   (a) *Preparation of **3***: To a stirred mixture of hydroxybenzoidoxole **2** (0.132 g, 0.5 mmol) in dichloromethane (10 ml), trimethylsilyl triflate (0.222 g, 1 mmol) and then pyridine (0.04 g, 0.5 mmol) were added. The color of the solution immediately changed from colorless to yellow. The reaction mixture was stirred at room temperature for an additional hour, then the resulting white, microcrystalline precipitate was collected by filtration, washed with ether and dichloromethane, and dried in vacuum to afford 0.14 g (57%) of pyridinium complex **3** as a monohydrate. Mp 210°C dec. IR (KBr): 3087, 1609, 1563, 1277, 1225, 1158, 1028 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3/CF_3COOH$, 20:1): δ 8.91 (d, 2H), 8.62 (t, 1H), 8.33 (dd, 1H), 8.13 (dt, 1H), 8.10 (t, 2H), 7.99 (dd, 1H), 7.86 (dt, 1H). Anal. calcd for $C_{13}H_{11}F_3INO_6S$: C, 31.66; H, 2.25; N, 2.84; I, 25.73; S, 6.50. Found: C, 31.59; H, 2.28; N, 2.91; I, 26.02; S, 6.62%. ES HRMS *m*/*z* (%): 264.936477 (100) [*M*–Py–OTf]$^+$, calcd for $C_7H_6IO_3$ 264.936171, and 343.978849 (15) [*M*–OTf]$^+$, calcd for $C_{12}H_{11}INO_3$ 343.978370.

   (b) *Preparation of **4***: Complex **4** was prepared by a similar procedure[6a] from hydroxybenzidoxole **2**, 1,1′-sulfonyldiimidazole, and trimethylsilyl triflate and was isolated as a monohydrate in 43% yield. Mp 190°C dec. IR (KBr): 3135 (br., NH), 3085, 1680, 1592, 1291, 1223, 1177, 1026 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.54 (br. s, 2H), 8.2–8.0 (m, 2H), 7.95 (br. s, 2H), 7.88 (m, 1H), 7.75 (m, 1H), 7.74 (m, 1H), 7.27 (br. s, 2H). Anal. calcd for $C_{15}H_{13}F_6IN_4O_{11}S_3$: C, 23.63; H, 1.72; S, 12.62. Found: C, 23.25; H, 1.49; S, 12.25%. ES MS *m*/*z* (%): 265 (100) [*M*–Py–OTf]$^+$, 463 (5) [*M*–OTf]$^+$.

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9. *Preparation of **6***: To a stirred mixture of bis(acetoxy)iodylbenzene[8] **5** (0.17 g, 0.5 mmol) in dichloromethane (10 ml), the solutions of trimethylsilyl triflate (0.444 g, 2 mmol) in dichloromethane (10 ml), and then 2,2′-bipyridyl (0.078 g, 0.5 mmol) in dichloromethane (10 ml), were added. The reaction mixture was stirred at room temperature for an additional hour and then concentrated in vacuum. Recrystallization of the residue from dichloromethane/hexane afforded 0.306 g (91%) of complex **6** as a white, microcrystalline solid. Mp 165°C dec. IR (KBr): 3102, 1617, 1290, 1254, 1171, 1031, 756 (I=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3/CF_3COOH$, 20:1): δ 9.18 (d, 2H), 8.91 (dd, 2H), 8.70 (d, 2H), 8.36 (dd, 2H), 8.10 (m, 2H), 7.84 (m, 3H). Anal. calcd for $C_{18}H_{13}F_6IN_2O_7S_2$: C, 32.06; H, 1.94; N, 4.15; S, 9.51. Found: C, 32.54; H, 2.15; N, 4.36; S, 9.22%. ES MS *m*/*z* (%): 157 (100) [*M*–PhIO–2TfO+H]$^+$, 525 (5) [*M*–OTf]$^+$.
10. It is interesting to note that the ^{1}H NMR spectrum of complex **6** shows only one set of pyridinium signals, while in a static structure **6** pyridinium rings of the bipyridyl ligand should be non-equivalent due to the iodine(V) geometry.[7] This equivalency of pyridinium rings is probably explained by a rapid exchange process on the NMR time scale.