Structure and Chemistry of Hypervalent Iodine Heterocycles: Acid-Catalyzed Rearrangement of Benziodazol-3-ones to 3-Iminiumbenziodoxoles

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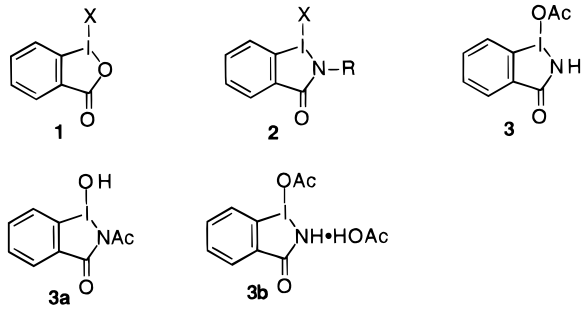
New 1-substituted benziodazoles, namely, azide **7**, tosylate **8**, mesylate **9**, and triflate **10**, were prepared by the reaction of acetoxybenziodazole **3** with $TMSN_3$, $TsOH·H_2O$, MsOH, or TMSOTf, respectively. Reaction of triflate **10** with alcohols (methanol, ethanol, 2-propanol, and 2-adamantanol) afforded novel 1-alkoxy-3-iminiumbenziodoxoles **11a**−**d**, while similar reactions with amides gave 1-amido-3-iminiumbenziodoxoles **12a**−**d** in 51−89% yield. The structure of iminiumbenziodoxole **12b** was established by a single-crystal X-ray analysis. The results of *ab initio* molecular orbital calculations on structures **3** and **11** are in good agreement with X-ray structural data. The calculation results indicate that the driving force of the novel rearrangement of benziodazoles to 3-iminiumbenziodoxoles is the greater thermodynamic stability of the *N*-protonated 3-iminobenziodoxoles relative to *O*-protonated benziodazol-3-ones by about 9.0 (MP2: 10.8) kcal/mol in the case of the acetoxy substituted **3** and **3d** compounds and 15 kcal/mol (MP2: 13.5 kcal/mol) for the methoxy-substituted derivatives **11** and **13**.

Introduction

There has been a significant recent interest in the five-membered iodine−oxygen heterocycles, benziodoxoles (**1**), due to their excellent catalytic activity in the cleavage of toxic phosphates and several useful applications as reagents for organic synthesis.[1−6] Particularly interesting was recent preparation of (alkylperoxy)benziodoxoles (**1**, X = OOR),[3] azidobenziodoxoles (**1**, X = N_3),[4,5] cyanobenziodoxoles (**1**, X = CN),[6] amidobenziodoxoles (**1**, X = HNAc),[7] and tosyloxybenziodoxoles (**1**, X = OTs).[8] (Alkylperoxy)benziodoxoles were found to be useful reagents for oxidation and deprotection of benzyl and allyl ethers[3] and azidobenziodoxoles were efficient azidating reagents;[4] cyano- and amidobenziodoxoles could be used for direct cyanation and amidation of organic substrates.[7,8] In contrast to benziodoxoles (**1**), the analogous five-membered iodine−nitrogen heterocycles, benziodazoles (**2**), have received much less attention, and moreover, their structural assignment in some cases was not reliable.[1,2b,5,9−11] The most important and readily available derivative of benziodazole, acetoxybenziodazole **3**, was first prepared in 1965 by peracetic oxidation of 2-iodobenzamide.[9] On the basis of IR spectroscopy, the authors of this paper[9] incorrectly assigned the structure of *N*-acetyl-1-hydroxy-3(1*H*)-1,2-benziodazol-3-one (**3a**) to this compound. Structure **3a** was also adopted in the more recent studies.[2b,5,10]



Recently we reported an X-ray crystal structure of acetate **3** (as a solvate with acetic acid, **3b**) and preliminary results on its chemical reactions including the novel

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(8) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Simonsen, A. J. *J. Org. Chem.* **1996**, *61*, 6547.

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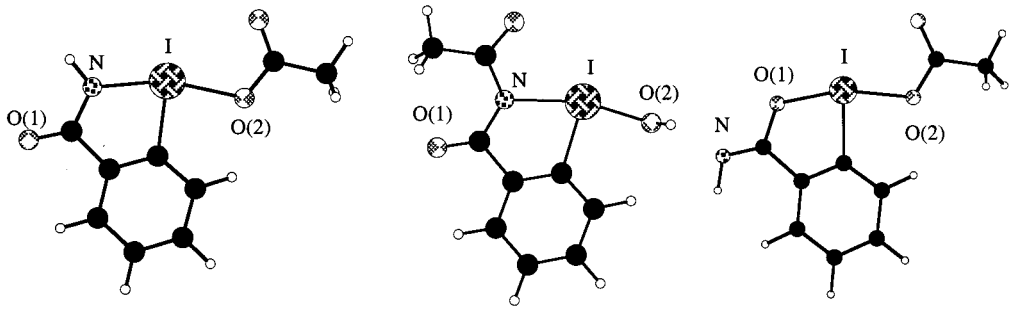
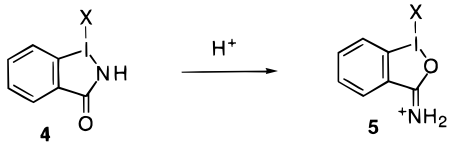


Figure 1. Calculated structures of the alternative compounds **3**, **3a**, and **3d**.

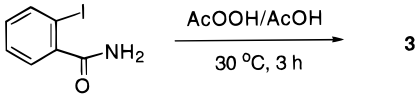
rearrangement of benziodazole **4** to iminobenziodoxoles **5** under acidic conditions.[12]



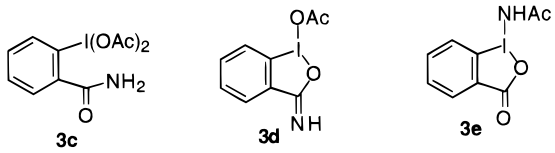
In this paper we report additional structural evidence and computational results on the geometry and stability of compounds **4** and **5** which will clarify the driving force for this novel rearrangement.

Results and Discussion

Acetoxybenziodazole **3** was prepared by oxidation of 2-iodobenzamide with peracetic acid according to the previously reported procedures.[2b,9]



An infrared spectrum of our sample was in good agreement with literature data.[2b,9] Specifically, the IR showed a broad absorption band of NH centered at 3100 cm^{-1}, which previously was incorrectly assigned to the hydroxyl group in an alternative structure **3a**,[9] and two carbonyl bands at 1661 and 1610 cm^{-1}. Elemental analysis and NMR spectra of our sample were consistent with structure **3**. Our sample of **3** had a melting point of 201−203 °C (with decomposition), which was higher than previously reported data on melting points for this compound, prepared by the same procedure: 143−145 °C dec[2b] and 140 °C dec.[9] Compared to the previously reported samples,[2b,9] our sample was additionally dried in high vacuum for several hours, which effectively removed water and acetic acid from the initially formed crystallosolvates causing the observed increase in melting point. Crystallization of **3** from a solution in acetic acid at room temperature afforded a solvate with one molecule of AcOH (**3b**) as was established by X-ray analysis.[12] The crystals of **3b**, initially obtained in the form of colorless needles, lost solvent upon extended drying in high vacuum to afford analytically pure **3** as a white microcrystalline powder. Barber and Henderson[10] used a slightly different procedure for peracetic oxidation of 2-iodobenzamide; they carried out oxidation at 50−60 °C and crystallized the product directly from acetic acid without treating it with water. Under these conditions, they obtained a sample in the form of colorless needles, which was assigned the structure of diacetate **3c** on the basis of elemental analysis.[10] Considering our X-ray data,[12] we assume that diacetate **3c** reported in this paper[10] has the actual structure of the isomeric acetoxybenziodazole **3b**.



In addition to structure **3a**, two more isomeric cyclic structures, namely, **3d** and **3e**, can be considered as alternative structures for acetoxybenziodazole **3**. One of these alternative structures, acetamidobenziodoxole **3e**, was recently prepared by the reaction of 2-iodosylbenzoic acid with acetamide in the presence of TMSOTf.[7] This compound (**3e**) has physical and spectroscopic characteristics distinctly different from our sample of **3**. Structures **3a** and **3d**, however, cannot be completely excluded as an alternative to structure **3**. To clarify this problem, we carried out molecular orbital calculations on all three alternative structures, **3**, **3a**, and **3d**. The geometries of all alternative structures were optimized at the Hartree−Fock level. The optimized structures were verified as minima by means of a vibrational analysis. All three structures were found to be minima on the potential surface. Single-point MP2 level calculations were performed to include correlation effects in the total energies. The structures of computational study are shown in Figure 1.

The calculations show that compound **3** has the highest stability among the three alternative structures. It is 6.31 kcal/mol more stable than **3a** and 17.95 kcal/mol more stable than **3d** at the Hartree−Fock level of theory. If correlation effects are included at the MP2 level of

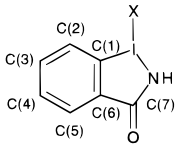
(12) Preliminary communication: Zhdankin, V. V.; Arbit, R. M.; McSherry, M.; Mismash, B.; Young, V. G. *J. Am. Chem. Soc.* **1997**, *119*, 7408.

Table 1. Energies of the Three Alternative Structures 3, 3a, and 3d[a]

structure	3	3a	3d
energy (HF)	−635.47527	−635.46521	−635.44666
energy (MP2)	−636.97049	−636.96671	−636.9416
ZPE, kcal/mol	106.349777	106.36607	106.424398
rel energy (HF)		+6.31	+17.95
rel energy (MP2)		+2.37	+18.13

[a] Absolute energies are in hartrees and Relative Energies (vs **3**) are in kcal/mol.

Table 2. Calculated and Experimental X-ray Structural Parameters of 1-Substituted Benziodazoles



	X = AcO		X = HO (**6**)	X = MeO (**16**)
	calcd (for **3**)	exptl (for **3b**)[12]	calcd	calcd
		Bond Lengths (Å)		
I−N	2.082	2.101 (5)	2.160	2.158
I−X	2.192	2.234 (4)	2.038	2.033
I−C(1)	2.114	2.106 (6)	2.112	2.112
N−C(7)	1.355	1.338 (7)	1.337	1.344
O−C(7)	1.206	1.246(8)	1.240	1.212
		Bond Angles (deg)		
N−I−C(1)	78.5	78.7 (2)	76.8	76.9
N−I−X	162.6	162.1 (2)	165.5	165.5
C(1)−I−X	84.1	83.4 (2)	88.7	88.6
C(7)−N−I	119.5	117.6(4)	119.0	119.3
C(6)−C(1)−I	112.2	111.9 (4)	114.0	114.0
N−C(7)−C(6)	110.4	112.5 (2)	110.9	110.3
N−C(7)−O	126.3	124.6 (6)	127.3	127.7

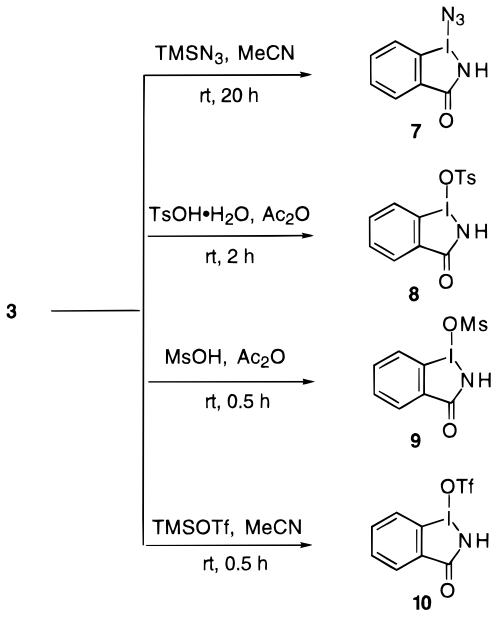
theory, **3** is 2.37 kcal/mol more stable than **3a** and 18.13 kcal/mol more stable than **3d** (Table 1). At the MP2 level of theory the difference in stability of the two structures **3** and **3a** is small, but overall, at the Hartree−Fock and MP2 levels of theory **3** is significantly more stable. Our results also show that **3d** is energetically strongly disfavored as a possible alternative structure.

Comparison of calculated structural parameters for **3** and X-ray data for the solvate **3b** (Table 2) shows good agreement. This good agreement is only achieved when the acetoxy group is used as a substituent on iodine. When a hydroxy (in structure **6**) or methoxy group (in structure **16**) is used, the structural parameters show less of an agreement, especially, the I−N distance. We attribute this to the electron-withdrawing effect of the acetoxy group and a more ionic nature of the I−O bond in **3** compared to **6** and **16**, which would cause a longer I−O distance and consequently a shorter I−N distance in **3**.

We optimized the geometries for several structures with the same ring structure around iodine but with different substituents in place of the acetoxy group. From these calculations it can be seen that replacing the acetoxy moiety simply by a hydroxy or methoxy group in calculations leads to discrepancies in I−N and I−O distances. The I−C distance is not much affected in a significant way by the change of substituents. Some angles are changed as well although the deviation from experimental values are not as dramatic as in the case of bond lengths (Table 2).

To further clarify the structure of **3** in the desolvated state and to get insight into its reactivity, we investigated its reactions with azidotrimethylsilane and sulfonic acids (Scheme 1).

Scheme 1



Acetoxybenziodazole **3** reacts at room temperature with azidotrimethylsilane to afford a novel azide **7** in the form of a yellow, microcrystalline precipitate. Product **7** was identified by elemental analysis and IR and ^{1}H NMR spectra. In particular, the IR spectrum of **7** displays a very intense peak of the azido function at 2034−2053 cm^{-1}, which is similar to the azido stretch in azidobenziodoxole[4] at 2048 cm^{-1}.

Acetoxybenziodazole **3** reacts with sulfonic acids or trimethylsilyl triflate affording the corresponding sulfonate derivatives **8**−**10** (Scheme 1). The reaction conditions vary in each case. Triflate **10** is best prepared by the reaction of **3** with trimethylsilyl triflate in acetonitrile at room temperature. Mesylate **9** slowly crystallizes from the solution of **3** in neat methanesulfonic acid in the form of large, colorless crystals, while tosylate **8** is obtained in the form of a white, microcrystalline precipitate in a slightly exothermic reaction of **3** with TsOH·H$_2$O in acetic anhydride. All three adducts are isolated as hygroscopic, but thermally stable, crystalline solids. The most stable to moisture is tosylate **8**; according to elemental analyses

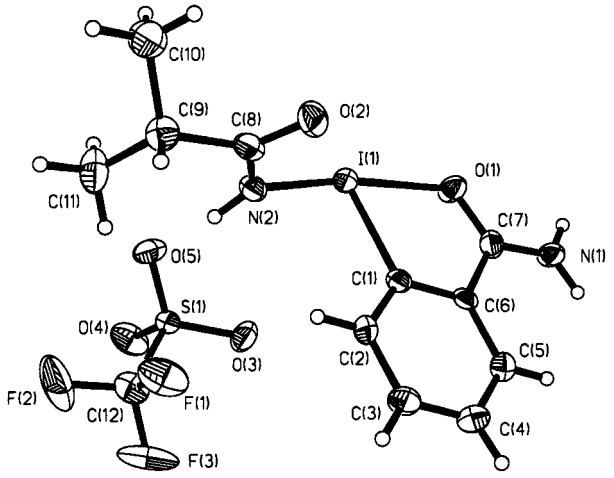
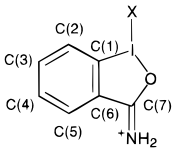


Figure 2. X-ray crystal structure of compound **12b**.

Table 3. Calculated and Experimental X-ray Structural Parameters of 1-Substituted 3-Iminiumbenziodoxoles

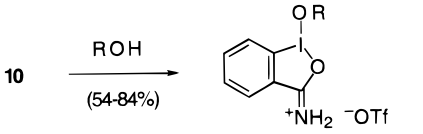


	X = *i*-PrO (**11c**)		X = *i*-PrOC(O)NH (**12b**)	X = AcO (**3d·H⁺**)
	calcd (for X = MeO)	exptl[12]	exptl	calcd
		Bond Lengths (Å)		
I−O	2.380	2.271 (2)	2.323 (3)	2.294
I−X	1.937	1.986 (2)	2.010 (4)	1.978
I−C(1)	2.128	2.107 (3)	2.104 (5)	2.126
N−C(7)	1.323	1.329 (4)	1.315 (6)	1.318
O−C(7)	1.237	1.276 (4)	1.267 (6)	1.244
		Bond Angles (deg)		
X−I−C(1)	91.8	91.86 (10)	94.8 (2)	93.0
X-I-O	164.9	167.88 (8)	170.06 (14)	167.2
Cl(1)-I-O	73.12	76.28 (9)	75.3 (2)	74.3
C(7)-O-I	115.3	113.9 (2)	113.8 (3)	116.4
C(6)-C(1)-I	117.6	114.9 (2)	116.5 (3)	116.0
O-C(7)-C(6)	116.8	116.9 (3)	117.2 (4)	116.3
N-C(7)-O	121.5	120.2 (3)	120.9 (5)	121.1
HF energy[a]	−523.13456		−635.85651	
MP2 energy[a]	−524.41571			−637.34330

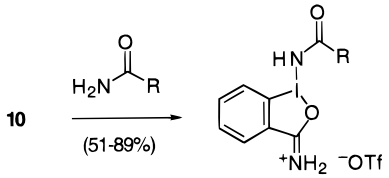
[a] Energies are in hartrees.

and spectral data it does not form crystallohydrates upon a brief exposure to an open air. Mesylate **9** and triflate **10** are highly hygroscopic and can be isolated only in the form of crystallohydrates.

Triflate **10** reacted with amides and alcohols at room temperature to afford rearranged products **11** and **12**.



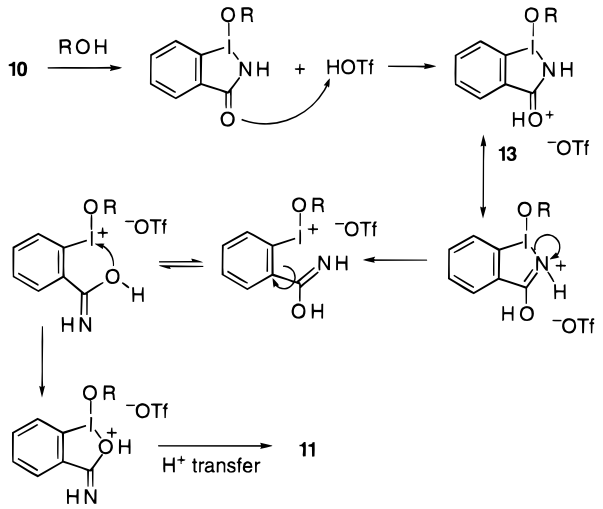
11a: R = Me
11b: R = Et
11c: R = *i*-Pr
11d: R = 2-Adamantyl



12a: R = Et
12b: R = *i*-Pr
12c: R = *t*-Bu
12d: R = Ph

The structures of the iminium salts **11c**[12] and **12b** (Figure 2) were unambiguously established by a single-crystal X-ray analysis; other products (**11**, **12**) were identified by elemental analysis and IR and ^{1}H NMR spectra. Specifically, ^{1}H NMR of amides **12** 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 ^{1}H NMR of the alkoxy derivatives **11**, the signals of the iminium protons were observed at about 8.6 and 8.5 ppm. Calculated and experimental X-ray structural parameters of 1-substituted 3-iminium-benziodoxoles are summarized in Table 3. In the case

Scheme 2



of the iminium salts, the agreement with the experimental data is not as good as for the nonprotonated species. We attribute this to the ionic structure of these compounds and their involvement in extensive hydrogen bonding in the solid state and to a different conformation of the 1-substituent. In the solid state these compounds have a coplanar arrangement of the 1-substituent.

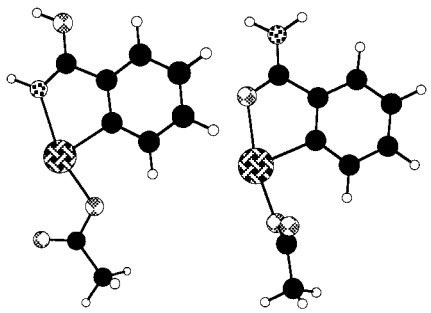
We also investigated the rearrangement from **10** to **11** by the same theoretical methods. A plausible mechanism of this rearrangement is shown in Scheme 2. The mechanism most likely includes ring opening and ring closure in the protonated benziodazole **13**.

We believe that the thermodynamic driving force for this novel rearrangement is the greater stability of the protonated imines **11** and **12** compared to the alternative protonated species **13**.

It can be generally observed that protonation at the exocyclic oxygen atom in **13** leads to an increase in the I−N bond length and a weakening of this bond. Subsequent rearrangement leads to the compounds with an exocyclic nitrogen. Proton transfer leads to the products which are isolated as the protonated iminium salt **11**.

We compared the energies of alternative protonated structures for the acetyl derivatives **3** and **3d** (Figure 3).

In the nonprotonated case the benziodazole, with an endocyclic nitrogen, is clearly favored by 18.0 kcal/mol at the HF level and 18.1 kcal/mol at the MP2 level of theory (Table 1). In the protonated case, however, the structure with an endocyclic oxygen and exocyclic nitro-

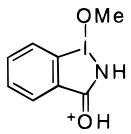


3•H⁺ **3d•H⁺**

Figure 3. HF level optimized structures of alternative protonated species **3**·H$^+$ and **3d**·H$^+$.

gen is preferred by 9.0 kcal/mol at the HF level and 10.8 kcal/mol at the MP2 level.

The same observation was made for the methyl-substituted compounds **14** and **15**. The protonated species are more stable with an endocyclic oxygen atom, in the case of **14** and **15** by 15.0 kcal/mol at the HF level and 13.5 kcal/mol at the MP2 level.



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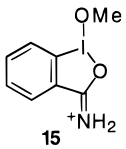

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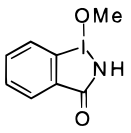
Compared to that, the nonprotonated species with the endocyclic nitrogen atom (**16**) is more stable than the alternative structure **17** by 6.3 kcal/mol at the HF and 8.1 kcal/mol at the MP2 level.



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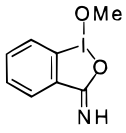

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Conclusion. In summary new 1-substituted benziodazoles (**7**−**10**) were prepared from acetoxybenziodazole **3**. Reaction of triflate **10** with alcohols afforded novel 1-alkoxy-3-iminiumbenziodoxoles **11a**−**d**, while similar reactions with amides gave 1-amido-3-iminiumbenziodoxoles **12a**−**d** in 51−89% yield. The structure of iminiumbenziodoxole **12b** was established by a single-crystal X-ray analysis. The results of *ab initio* molecular orbital calculations on structures **3**, **11**, and **12** are in good agreement with X-ray structural data. The calculation results indicate that the driving force of the novel rearrangement of benziodazoles to 3-iminiumbenziodoxoles is the greater thermodynamic stability of the *N*-protonated 3-iminobenziodoxoles relative to *O*-protonated benziodazol-3-ones by about 15 kcal/mol (HF level) and 13.5 kcal/mol (MP2 level).

Experimental Section

Computational Details. All calculations were performed using the program GAMESS.[13] For iodine the effective core potential basis by Hay and Wadt was used.[14] For all remaining atoms, double-ζ basis sets of Dunning and Hay were used.[15] These were augmented with *d* polarization functions for the atoms that are bonded to iodine (ζ = 1.292 for O, 0.626 for C, and 0.913 for N). Atoms that were not bonded to iodine in one structure but had a bond in an isomeric structure (such as the imine nitrogen atom or the carbonyl oxygen atom) were also augmented with *d* polarization functions in order to maintain the same overall basis set for different isomers. Geometry optimizations were performed at the Hartree−Fock level and single-point MP2 energies with frozen core electrons. Several combinations of basis sets were examined, but the listed basis set combination gave the best agreement for the structures with experimental geometries.[16]

All refined structures were confirmed as minima on the potential energy surface by a vibrational analysis. Plots of the structures were made using the program MacMolPlt by Brett Bode at Iowa State University.

General. All melting points were determined in an open capillary tube and are uncorrected. Infrared spectra were recorded neat, as a CCl_4 mull, or as a KBr pellet. NMR spectra were recorded at 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR), and 282.2 MHz (^{19}F NMR). Chemical shifts are reported in parts per million (ppm), ^{1}H chemical shifts are referenced to the proton resonance due to the residual protons in the deuteriated NMR solvent, and ^{19}F chemical shifts are given relative to external $CFCl_3$. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

Materials. All commercial reagents were ACS reagent grade and used without further purification. 2-Iodobenzamide was prepared from commercial 2-iodobenzoyl chloride (Aldrich) by a known method.[3] Trimethylsilyl triflate was prepared from triflic acid (3M Company) and fresh-distilled trimethylsilyl chloride, additionally purified by a fractional distillation. Peracetic acid (32% solution in acetic acid) was purchased from Aldrich Chemical Co. Methylene chloride, hexane, and acetonitrile were distilled from CaH_2 immediately prior to use. Diethyl ether was distilled from Na/benzophenone. All other reagents and solvents were of commercial quality from freshly opened containers. Reaction flasks were oven-dried at 200 °C, flame-dried and flushed with dry nitrogen prior to use.

1-Acetoxy-1,2-benziodazol-3(1*H*)-one 3. To a mixture of 2-iodobenzamide (10 g, 40.5 mmol) in 75 mL of glacial acetic acid was added 32% peracetic acid (24 mL, 109 mmol) with stirring. The addition was carried out slowly to avoid the intensive reacting, and the temperature was maintained at 30 °C. The mixture was additionally stirred for 3 h under ambient conditions; then the white precipitate was filtered and washed with cold water (3 × 50 mL) and then washed with ice-cold methanol (10 mL) and dried on the filter. It was then washed with ether (150 mL) and dried in vacuum to give 6.42 g (52%) of acetate **3**: mp 201−203 °C dec (lit. data: mp 192−193 °C dec,[10] 143−145 °C dec,[2b] 140 °C dec[9]); IR (KBr) 3100 (br, NH), 3090, 2925, 2875, 1661, 1610 cm^{-1} (lit. data: IR 3100, 1666, 1618 cm^{-1});[2b,9] ^{1}H NMR ($CDCl_3$/DMSO-d_6, 20:1) δ 8.25 (d, 1H, J = 8 Hz), 8.08 (d, 1H, J = 8 Hz), 7.80 (dd, 1H, J = 8 Hz), 7.68 (t, 1H, J = 8 Hz), 7.37 (br s, exchangeable with D_2O, 1H, NH), 2.21 (s, 3H). Anal. Calcd for $C_9H_8INO_3$: C, 35.43; H, 2.64; N, 4.59. Found: C, 35.47; H, 2.60; N, 4.49. X-ray crystal structure of **3** as a solvate with a molecule of acetic acid was reported in our preliminary communication.[12]

1-Azido-1,2-benziodazol-3(1*H*)-one 7. To the mixture of acetate **3** (0.305 g, 1 mmol) in 10 mL of dry acetonitrile was added trimethylsilyl azide (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 and dried in vacuum to give 0.170 g (61%) of azide **7**: mp 122 °C dec, explodes); IR (KBr) 3200 (br, NH), 3083, 3065, 2053, 2034 (N_3), 1613 cm^{-1}; 1H NMR (DMSO-d_6) δ 8.5 (br s, exchangeable with D_2O, 1H, NH), 8.15 (d, 1H, J = 8 Hz), 7.98 (m, 2H), 7.79 (dd, 1H, J = 8 Hz). Anal. Calcd for $C_7H_5IN_4O$: C, 29.19; H, 1.75; N, 19.45. Found: C, 29.28; H, 1.72; N, 19.35. CAUTION: azidobenziodazole **7** decomposes with an explosion upon heating to 122 °C and should be handled with care.

1-(*p*-Toluenesulfonyloxy)-1,2-benziodazol-3(1*H*)-one 8. To a stirred mixture of acetate **3** (0.305 g, 1 mmol) in 5 mL of acetic anhydride was added TsOH·H_2O (0.290 g, 1.5 mmol) at room temperature. After 10 min of stirring, a slightly exothermic reaction began. The solution was additionally stirred for 2 h until a white microcrystalline precipitate formed. Then the reaction mixture was diluted with 20 mL of dry ether, and the precipitate was filtered and washed with 3 × 10 mL of anhydrous ether and dried in vacuum to afford analytically pure product **8**: yield 0.373 mg (90%); mp 187−188 °C dec; IR (KBr) 3200 (br, NH), 3098, 2921, 1663, 1442, 1279, 1250, 1120, 1027 cm^{-1}; ^{1}H NMR ($CDCl_3$/DMSO-d_6, 20:1) δ 9.45−8.65 (br

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s, exchangeable with D_2O, NH), 8.5 (d, 1H, J = 8 Hz), 8.15 (dd, 1H, J = 8 Hz), 7.94 (d, 1H, J = 8 Hz), 7.80 (dd, 1H, J = 8 Hz), 7.71 (d, 2H, J = 8 Hz), 7.29 (d, 2H, J = 8 Hz), 2.40 (s, 3H). Anal. Calcd for $C_{14}H_{12}INO_4S$: C, 40.30; H, 2.90; N, 3.36. Found: C, 40.06; H, 2.87; N, 3.24.

1-(Methanesulfonyloxy)-1,2-benziodazol-3(1*H*)-one 9. The starting acetate **3** (0.305 g, 1 mmol) was dissolved in 1 mL of neat methanesulfonic acid at room temperature with stirring. Then dry acetonitrile (1 mL) and anhydrous ether (1 mL) were added, and the resulting solution was left for several hours at 0 °C for crystallization of the product. Colorless crystals of product **9** were filtered, washed with anhydrous ether, and dried in vacuum: yield 0.264 g (84%); mp 167-169 °C dec; IR (KBr) 3300−3200 (br, NH), 3098, 2921, 1663, 1613, 1337, 1206, 1149, 1039 cm^{-1}; ^{1}H NMR (CD_3CN/DMSO-d_6, 20:1) δ 9.85-9.20 (br s, exchangeable with D_2O, NH), 8.61 (d, 1H, J = 8 Hz), 8.45 (dd, 1H, J = 8 Hz), 8.05 (d, 1H, J = 8 Hz), 7.90 (dd, 1H, J = 8 Hz), 2.99 (s, 3H). Anal. Calcd for $C_8H_8INO_4S\cdot H_2O$: C, 26.76; H, 2.81; N, 3.90. Found: C, 26.32; H, 2.75; N, 3.73.

1-(Trifluoromethanesulfonyloxy)-1,2-benziodazol-3(1*H*)-one 10. To the slurry of acetate **3** (0.633 g, 2.08 mmol) in 15 mL of dry acetonitrile under nitrogen and with stirring was added TMSOTf (0.405 mL, 2.08 mmol) 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 to afford the analytically pure triflate in the form of a fine powder, yield 0.789 g (96%); mp 110−115 °C. Product **10** is highly hygroscopic. After exposure to the air, the original yellow solid turned into a white, microcrystalline hydrate: IR (KBr) 3300-3200 (br, NH), 3090, 1674, 1271, 1233, 1166, 1024 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.7−8.5 (br s, exchangeable with D_2O, NH), 8.20 (d, 1H, J = 8 Hz), 7.95 (m, 2H), 7.79 (dd, 1H, J = 8 Hz); ^{19}F NMR (CD_3CN) δ −79.73 (OTf); ^{13}C NMR (CD_3CN) δ 172.7, 138.0, 132.5, 131.2, 127.6, 125.3, 121.0, 121.5 (q, J = 318 Hz, OTf). Anal. Calcd for $C_8H_5F_3INO_4S\cdot H_2O$: C, 26.76; H, 2.81; N, 3.90. Found: C, 26.32, H, 2.75, N, 3.73.

Reactions of Triflate 10 with Alcohols (General Procedure). Freshly prepared triflate **10** (0.40 g, 1 mmol) was dissolved in 5 mL of dry acetonitrile, and 1−1.5 mL of the appropriate anhydrous alcohol was added. The color of the solution immediately changed from yellow to colorless. The solution was stirred for an additional 1 h; then the solvent was evaporated to give white crystals, which were recrystallized by dissolving in minimum volume of acetonitrile or appropriate alcohol and addition of ether. The white microcrystalline precipitate of the alkoxy derivative **11** was filtered, washed with 2 × 10 mL of ether, and dried in vacuum.

1-Methoxy-3(1*H*)-1,2-benziodoxole-3-iminium triflate 11a was obtained according to the general procedure by addition of 1 mL of anhydrous methanol. Recrystallization from methanol gave 0.36 g (84%): mp 163−167 °C; IR (KBr) 3300−3200 (br), 3095, 2949, 1656, 1271, 1245, 1165, 1020 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.62 and 8.55 (2br s, exchangeable with D_2O, NH_2), 8.45 (d, 1H, J = 8 Hz), 8.20 (dd, 1H, J = 8 Hz), 8.05 (d, 1H, J = 8 Hz), 7.95 (dd, 1H, J = 8 Hz), 4.45 (s, 3H); ^{19}F NMR (CD_3CN) δ −79.2. Anal. Calcd for $C_9H_9F_3INO_5S$: C, 25.31; H, 2.12; N, 3.28. Found: C, 25.05; H, 2.08; N, 3.24.

1-Ethoxy-3(1*H*)-1,2-benziodoxole-3-iminium triflate 11b was obtained according to the general procedure by addition of 1 mL of anhydrous ethanol. Recrystallization from ethanol gave 0.362 g (82%): mp 161−163 °C; IR (KBr) 3300−3200 (br), 3095, 2959, 1656, 1271, 1245, 1165, 1020 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.6 and 8.5 (2br s, exchangeable with D_2O, NH_2), 8.45 (d, 1H, J = 8 Hz), 8.20 (dd, 1H, J = 8 Hz), 8.05 (d, 1H, J = 8 Hz), 7.95 (dd, 1H, J = 8 Hz), 4.50 (q, 2H, CH_2), 1.45 (t, 3H); ^{19}F NMR (CD_3CN) δ −79.2. Anal. Calcd for $C_{10}H_{11}F_3INO_5S$: C, 27.23; H, 2.51; N, 3.17. Found: C, 27.32; H, 2.47; N, 3.16.

1-Isopropyloxy-3(1*H*)-1,2-benziodoxole-3-iminium triflate 11c was obtained according to the general procedure by addition of 1.5 mL of anhydrous 2-propanol: 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}; ^{1}H NMR (CD_3CN) δ 8.6 and 8.5 (2br s, NH_2), 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); ^{19}F NMR (CD_3CN) δ −78.90; ^{13}C NMR (CD_3CN) δ 172.6, 137.7, 132.4, 131.1, 127.4, 126.3, 121.0, 121.5 (q, J = 318 Hz, OTf), 64.4, 25.1. Anal. Calcd for $C_{11}H_{13}F_3INO_5S$: C, 29.03; H, 2.88; N, 3.08. Found: C, 28.97; H, 2.84; N, 3.04. X-ray crystal structure of compound **11c** was reported in our preliminary communication.[12]

1-(2-Adamantyloxy)-3(1*H*)-1,2-benziodoxole-3-iminium triflate 11d was obtained according to the general procedure by addition of 0.198 g (1.3 mmol) of 2-adamantanol in 5 mL of CH_2Cl_2. After workup 0.294 g (54%) of **7d** was obtained: mp 171−172 °C (from CH_3CN); IR (KBr) 3300−3200 (br), 3095, 2907, 1667, 1287, 1235, 1165, 1020 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.55 and 8.35 (2br s, exchangeable with D_2O, NH), 8.30 (d, 1H, J = 8 Hz), 8.13 (dd, 1H, J = 8 Hz), 8.97 (d, 1H, J = 8 Hz), 7.91 (dd, 1H, J = 8 Hz), 4.32 (br s, 1H, CH), 2.1−1.5 (m, 14H, Ad); ^{19}F NMR (CD_3CN) δ −79.1. Anal. Calcd for $C_{18}H_{21}F_3INO_5S$: C, 39.50; H, 3.87; N, 2.56. Found: C, 38.96; H, 3.82; N, 2.51.

Reactions of Triflate 10 with Amides (General Procedure). Freshly prepared triflate **10** (0.40 g, 1 mmol) was dissolved in 5 mL of dry acetonitrile, and a solution of 1.5 mmol of the appropriate amide in 1−3 mL of dry dichloromethane was added. The color of the solution changed from yellow to colorless. The solution was stirred for an additional 1 h; then the solvent was evaporated to give white crystals of **12**, which were recrystallized from acetonitrile.

1-Propanamido-3(1*H*)-1,2-benziodoxole-3-iminium triflate 12a was prepared according to the general procedure in 51% yield: mp 158−160 °C (from CH_3CN); IR (KBr) 3369 and 3229 (br), 3095, 2994, 1676, 1661, 1292, 1223, 1165, 1015 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.34 and 8.30 (2br s, exchangeable with D_2O, NH_2), 8.23 (d, 1H, J = 8 Hz), 7.98 (dd, 1H, J = 8 Hz), 7.84 (d, 1H, J = 8 Hz), 7.72 (br s, exchangeable with D_2O, NH), 7.57 (dd, 1H, J = 8 Hz), 2.75 (q, 2H), 1.35 (t, 3H); ^{19}F NMR (CD_3CN) δ −79.2. Anal. Calcd for $C_{11}H_{12}F_3IN_2O_5S$: C, 28.22; H, 2.58; N, 5.98. Found: C, 28.03; H, 2.53; N, 5.80.

1-(2-Methylpropanamido)-3(1*H*)-1,2-benziodoxole-3-iminium triflate 12b was prepared according to the general procedure in 66% yield: mp 175−177 °C (from CH_3CN); IR (KBr) 3351 and 3229 (br), 3095, 2978, 1679, 1667, 1290, 1224, 1163, 1010 cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.40 and 8.35 (2br s, exchangeable with D_2O, NH_2), 8.23 (d, 1H, J = 8 Hz), 7.97 (dd, 1H, J = 8 Hz), 7.84 (d, 1H, J = 8 Hz), 7.72 (br s, exchangeable with D_2O, NH), 7.67 (dd, 1H, J = 8 Hz), 2.95 (septet, 1H, CH), 1.24 (d, 6H); ^{19}F NMR (CD_3CN) δ −79.2. Anal. Calcd for $C_{12}H_{14}F_3IN_2O_5S$: C, 29.89; H, 2.93; N, 5.81. Found: C, 29.92; H, 2.89; N, 5.77. X-ray quality single crystals of **12b** were obtained by slowly crystallizing a solution of **7c** in acetonitrile in a refrigerator. Crystal data for **12b** (173 K, Mo Kα radiation, Siemens SMART Platform CCD diffractometer): $C_{12}H_{14}F_3IN_2O_5S$, FW = 482.21, a = 11.3550(6) Å, b = 13.2100(7) Å, c = 11.6288(6) Å, β = 97.951(1)°, monoclinic, $P2_1/n$, Z = 4, V = 1727.5(2) Å^3, D_c = 1.854 g cm^{-3}. R factor = 0.0392 for 2373 independent observed reflections ($I > 2\sigma(I)$); weighted R^2 factor = 0.0849. Selected bond lengths and bond angles of structure **12b** are listed in Table 2. Further details on the crystal structure of **12b** are available in the Supporting Information.

1-(2,2-Dimethylpropanamido)-3(1*H*)-1,2-benziodoxole-3-iminium triflate 12c was prepared according to the general procedure in 89% yield: mp 181−183 °C (from CH_3CN); IR (KBr) 3347 and 3227 (br), 3095 (Ar), 2975, 1669, 1651, 1292, 1223, 1165, 1015 cm^{-1}; ^{1}H NMR (CD^3CN) δ 8.34 and 8.30 (2br s, NH_2), 8.23 (d, 1H, J = 8 Hz), 7.98 (dd, 1H, J = 8 Hz), 7.84 (d, 1H, J = 8 Hz), 7.72 (br s, NH), 7.57 (dd, 1H, J = 8 Hz), 1.33 (s, 9H); ^{19}F NMR (CD_3CN) δ −79.2. Anal. Calcd for $C_{13}H_{16}F_3IN_2O_5S$: C, 30.78; H, 3.44; N, 5.98. Found: C, 31.09; H, 3.23; N, 5.62.

1-Benzamido-3(1*H*)-1,2-benziodoxole-3-iminium triflate 12d was prepared according to general procedure in 70% yield: mp 163−165 °C (from CH_3CN); IR (KBr) 3341 and 3174 (br), 3095, 1673, 1648, 1288, 1225, 1165, 1015 cm^{-1}; ^{1}H NMR

(CD_3CN) δ 8.96 (br s, exchangeable with D_2O, NH), 8.49 and 8.39 (2br s, exchangeable with D_2O, NH_2), 8.25 (d, 1H, $J = 8$ Hz), 8.09 (dd, 1H, $J = 8$ Hz), 8.0−7.5 (m, 7H); ^{19}F NMR (CD_3CN) δ −79.2. Anal. Calcd for $C_{15}H_{12}F_3IN_2O_5S$: C, 34.90; H, 2.34; N, 5.43. Found: C, 34.11; H, 2.28; N, 5.26.

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Supporting Information Available: Computational results, including Cartesian coordinates with computed total energies and molecular drawings, for compounds **3**, **3a**, **3d**, **6**, and **14**−**17**; X-ray crystallographic report for compound **12b** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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