Preparation, X-ray Crystal Structure, and Chemistry of Stable Azidoiodinanes−Derivatives of Benziodoxole

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Abstract: Azidoiodinanes **2** and **4a,b** can be prepared from the appropriate benziodoxoles **1** and **3a,b** and trimethylsilyl azide in the form of stable, crystalline compounds. A single-crystal X-ray analysis for azide **4b** revealed the expected hypervalent iodine distorted T-shaped geometry with the N1−I−O bond angle of 169.5 (2) degrees. The lengths of the bonds to the iodine atom, I−N (2.18 Å), I−O (2.13 Å), and I−C (2.11 Å), are within the range of typical single covalent bonds in organic derivatives of polyvalent iodine, while the previously reported benziodoxoles generally have an elongated I−O bond. The geometry of the $I^{(III)}$NNN fragment in **4b** is similar to the literature electron diffraction data on monomeric iodine azide, IN_3, in gas phase. Azidobenziodoxoles **2,4** are potentially useful reagents for direct azidation of organic substrates, such as dimethylanilines, alkanes, and alkenes. Reaction of **2** with dimethylanilines proceeds under mild conditions to afford the respective *N*-azidomethyl-*N*-methylanilines in excellent yield. Alkanes, cycloalkanes, and adamantanes react with azidobenziodoxoles **2** or **4b** in the presence of radical initiators at 80−132 °C with the formation of tertiary alkylazides, while reaction of norbornane leads to *exo*-2-azidonorbornane. Under similar conditions cyclohexene is selectively azidated at the allylic position.

Introduction

Covalent inorganic azides have attracted considerable current interest in both theoretical and practical aspects.[1] Iodine azide, IN_3, the first and the most important member of the family of halogen azides, was first prepared about 100 years ago[2] and found wide practical application in both organic and inorganic syntheses.[1,3] In pure form iodine azide is thermally unstable and highly explosive, which makes its structural identification difficult.[1−4] Despite significant interest in iodine azide for almost a century, it was only in 1993 that Klapötke, Schleyer, White, and co-workers succeeded in its X-ray structure characterization.[4a] In particular, it was found that in solid state IN_3 has polymeric structure with the average I−N distance of 2.3 Å.[4a] In gas phase, however, it has monomeric structure as determined by electron diffraction analysis.[4b]

Much less is known about the structure of azides of polyvalent iodine. Azidoiodinanes, $PhI(N_3)X$ (X = OAc, Cl, OTMS, etc.) or $PhI(N_3)_2$, were proposed as reactive intermediates in the widely used azidation reactions involving the combination of PhIO or $PhI(OAc)_2$ with trimethylsilyl azide or NaN_3.[5−9] Attempts to isolate these intermediates always resulted in fast decomposition at −25 °C to 0 °C with the formation of iodobenzene and dinitrogen;[5] however, low temperature spectroscopy[6a] and the subsequent chemical reactions in situ provided some experimental evidence toward the existence of these species.[6−9] The first systematic study of the structure and reactivity of the unstable, acyclic azidoiodinanes was attempted by Zbiral and co-workers in the early 1970s.[6] In particular, the IR spectroscopic measurements at −60 to 0 °C indicated the existence of $PhI(OAc)_{2-n}(N_3)_n$ species in the mixture of $PhI(OAc)_2$ with trimethylsilyl azide.[6a]

The unstable and highly reactive azidoiodinanes generated in situ from PhIO/$TMSN_3$, $PhI(OAc)_2/NaN_3$, or $PhI(OAc)_2/TMSN_3$ have found some practical application as efficient reagents for the introduction of the azido function into organic molecules.[6−9] For example, reaction of the $PhI(OAc)_2/TMSN_3$ or PhIO/NaN_3 systems with alkenes lead to diazides, α-azidoketones, or nitriles.[6,7] Treatment of *β*-dicarbonyl compounds with PhIO/$TMSN_3$ in chloroform affords the respective azides in moderate to good yield.[7a] Under similar conditions, 2-(tri-

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methylsiloxy)furan gives azidofuranone as the main product.[7b] Allyl azides can be prepared from alkyltrimethylsilanes utilizing the PhIO/$TMSN_3$/$BF_3{\cdot}Et_2O$ combination.[8a] Alkenes react with $PhI(OAc)_2$/$TMSN_3$ in the presence of diphenyl diselenide to produce vicinal azidoselenides in good yield.[8b] 3-Deoxyglycals can be converted into azidoglycals upon treatment with PhIO/$TMSN_3$.[8c] Aromatic compounds, such as anisoles and alkylbenzenes, can be azidated in the ring by treatment with $PhI(OCOCF_3)_2$/$TMSN_3$.[8d]

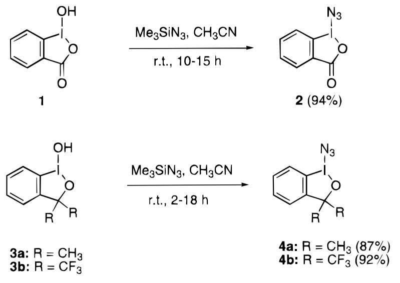
Recently Magnus and co-workers reported several new, synthetically useful azidations with the PhIO/MSN_3 combination, which serves presumably as the source of nonisolable azidoiodinanes $PhI(N_3)_2$ or $PhI(N_3)OTMS$.[9] Various triisopropylsilyl enol ethers react with this reagent at −15 to −18 °C to give the β-azido adducts in excellent yields.[9a,b] Likewise, *N*,*N*-dimethylarylamines are cleanly converted into azidomethylene derivatives with the PhIO/$TmSN_3$ reagent combination.[9c] Amides, carbamates, and ureas also can be α-azidated under similar conditions; however, the yields of azides in this case are generally lower.[9d]

It should be emphasized that the low thermal stability of the reported PhIO/$TMSN_3$ reagent combination restricts its practical application only to low temperature reactions with the most reactive organic substrates.

In this paper we wish to report the preparation, X-ray structure, and chemical reactivity of novel, stable azidoiodinanes **2** and **4a,b**.[10] The higher thermal stability of these compounds is achieved due to incorporation of polyvalent iodine into a five-membered heterocycle.[11]

Results and Discussion

Azidoiodinanes **2** and **4a,b** were synthesized in one step by the reaction of benziodoxoles **1** and **3a,b** with trimethylsilyl azide in acetonitrile. All three azidoiodinanes (**2,4a,b**) were isolated as thermally stable, yellow, crystalline solids. Azides **2** and **4b** have melting/decomposition points at 140−150 °C and can be stored at room temperature for several months without noticeable decomposition. Azide **4a** has lower thermal stability; however, it can be stored for several months in a refrigerator. Specially performed thermal and shock tests did not reveal any explosive properties for crystalline products **4**; however, azidoiodinane **2** decomposed with explosion upon heating to 138−140 °C.



1

2 (94%)

3a: R = CH_3
3b: R = CF_3

4a: R = CH_3 (87%)
4b: R = CF_3 (92%)

Azidoiodinanes **2,4a,b** were identified by spectral data, elemental analyses, and X-ray data (for **4b**). Specifically, IR spectra of all three compounds (**2,4a,b**) displayed a very intense peak of the azido function at 2048, 2034, and 2046 cm^{-1}, respectively. These IR data are in good agreement with the previously reported stretching vibrations of the azido-group in IN_3[12] at 2045 cm^{-1} and in $PhI(OAc)_{2-n}(N_3)_n$[6a] at 2040 cm^{-1}. The ^1H and ^{13}C NMR spectra of compounds **2,4a,b** showed signals and splitting patterns typical of *o*-substituted benzene rings and consistent with the proposed structures.

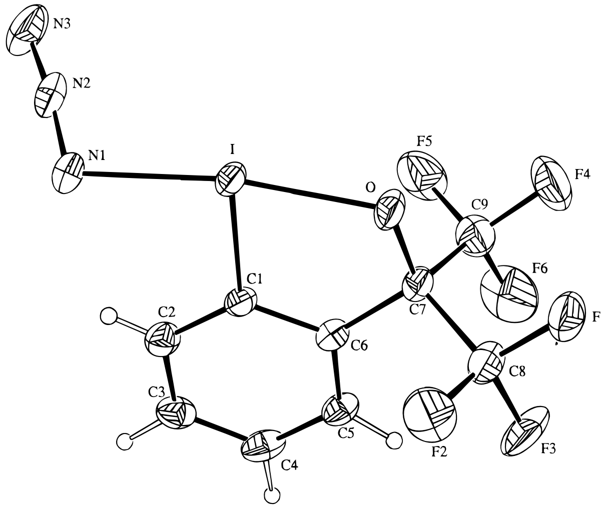


Figure 1. ORTEP representation of the molecular structure of azidobenzodoxole **4b**.

Table 1. Selected Bond Distances for **6**[a]

	distance (Å)		distance (Å)
I−O	2.130 (5)	N2−N3	1.12 (1)
I−N1	2.182 (7)	C6−C7	1.52 (1)
I−C1	2.109 (7)	C1−C6	1.38 (1)
O−C7	1.378 (9)	C7−C8	1.57 (1)
N1−N2	1.26 (1)	C7−C9	1.50 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2. Selected Bond Angles for **6**[a]

	angle (deg)		angle (deg)
O−I−N1	169.5 (2)	I−C1−C2	122.2 (6)
O−I−Cl	78.9 (2)	I−C1−C6	114.3 (5)
N1−I−C1	90.6 (3)	C1−C6−C7	117.5 (7)
I−O−C7	116.1 (4)	O−C7−C6	112.9 (6)
I−N1−N2	109.5 (6)	O−C7−C8	105.3 (7)
N1−N2−N3	174.0 (9)	O−C7−C9	107.1 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The structure of azide **4b** was unambiguously established by a single-crystal X-ray analysis. The ORTEP diagram is shown in Figure 1, and selected bond distances and bond angles are listed in Tables 1 and 2. The structural data revealed the expected hypervalent iodine distorted T-shaped geometry with the N1−I−O bond angle of 169.5 (2) degrees. The lengths of the bonds to the iodine atom, I−N (2.18 Å), I−O (2.13 Å), and I−C (2.11 Å), all have similar values, and generally are within the range of typical single covalent bonds in organic derivatives of polyvalent iodine.[11a] However, the endocyclic I−O bond in **4b** is significantly shorter than usual in iodine heterocycles, while the I−C and the I−N bonds are slightly longer. For example, the I−N bond length in benziodazoles[13] is 2.06−2.14 Å, while the endocyclic I−O bond in 1-alkynyl-1,2-benziodoxole-3(1*H*)-one[14a] has a distance of 2.34 Å and the I−C(1) bond length of 2.03 Å. An even greater difference in I−O (2.478

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Å) and I−C (2.105 Å) bond distances is observed in 1-phenyl-1,2-benziodoxole-3(1*H*)-one,[14b] which is more consistent with an open zwitterionic structure for this compound in contrast with cyclic structure of **4b**.

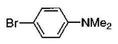
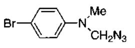
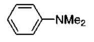
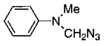
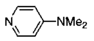
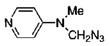
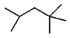
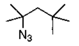
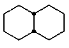
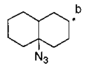
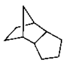
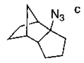
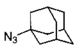
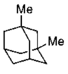
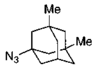
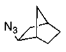
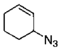
A comparison of our data on the geometry of the I$^{(III)}$NNN fragment in **4b** with the literature X-ray data on iodine azide reveals significant structural differences between these two compounds in solid state.[4a] In particular, in the solid state IN_3 forms zigzag polymeric −I−N(1)−I−(N1)− chains with the I−N(1) distance at 2.26−2.30 Å, the N(1)−I−N(1) bond angle of 177°, and the I−N(1)−N(2) bond angle of 114−117°,[4a] while azidoiodinane **4b** has a monomeric structure. However, the structure of the free IN_3 molecule[4b] determined by gas-phase electron diffraction analysis is in better agreement with our data on **4b**. According to the literature data,[4b] the monomeric IN_3 has the I−N(1) distance of 2.12 Å, the I−N(1)−N(2) bond angle of 106°, and the N−N−N bond angle of 169°, which is close to the respective calculated parameters[4a,15] of 2.12−2.13 Å, 110°, and 171°. Compared to the monomeric IN_3, azidoiodinane **4b** has a slightly elongated I−N bond, while the rest of the structural parameters are very similar. The relatively long I−N bond in **4b** can be ascribed to the stronger polarity of this bond in comparison with the monomeric IN_3.

Further perusal of X-ray structural data on **4b** reveals the presence of secondary bonding between the oxygen atom of the five-membered ring and the iodine atom of another molecule of **4b** with the I···O distance 3.030 Å. In addition to the I···O interaction, there exists a weaker intermolecular I···F interaction with the distance of 3.284 Å. A similar secondary bonding was observed in the previously reported benziodoxoles.[14]

Similarly to the unstable azidoiodinanes,[6−9] azidobenziodoxoles **2** and **4** can be used as efficient azidating reagents toward various organic substrates (Table 3). In a typical example, reagent **2** reacts with *N*,*N*-dimethylanilines **5** in dichloromethane at reflux in 30 min to afford the respective *N*-azidomethyl-*N*-methylanilines **6** in excellent yield. The analogous reaction of *N*,*N*-dimethylanilines with the PhIO/$TMSN_3$ system[9c] proceeds smoothly at −20 °C, which indicates lower reactivity of reagent **2** in comparison with the unstable $PhI(N_3)_2$ and $PhI(N_3)OTMS$. Azidoiodinanes **4a** and **4b** are even less reactive in this azidation reaction. Thus, the reaction of **4b** requires 3 h of reflux in dichloromethane, while reagent **4a** reacts with *N*,*N*-dimethylanilines only at relatively high temperature, upon reflux in 1,2-dichloroethane (bp 83 °C), to afford the respective products **6** in a moderate yield. Azidation of *N*,*N*-dialkylanilines by the 2-iodosylbenzoic acid/$TMSN_3$ system was previously reported by Magnus.[9b] Plausible mechanism for azidation of *N*,*N*-dimethylanilines with azidoiodinanes involves iminium cations as key intermediates.[9c]

The main advantage of reagents **2** and **4** over the known, unstable PhIO/$TMSN_3$ reagent combination is high thermal stability allowing its use at higher temperatures. We have found that the most stable azidoiodinanes **2** and **4b** can even be used for direct azidation of hydrocarbons at high temperatures and in the presence of radical initiators (Table 3). Azidoiodinane **2** selectively reacts with isooctane **7** upon reflux in 1,2-dichloroethane in the presence of catalytic amounts of benzoyl peroxide to afford tertiary azide **8** and 2-iodobenzoic acid as the only products according to NMR spectra of the reaction mixture. The individual azide **8** can be easily isolated in a good preparative yield by filtration of the reaction mixture through a short silica gel column using hexane as the eluent. Azidoiodinane **4b** can also react with isooctane **7** under these conditions, but the yield of azide **8** is substantially lower, and the unreacted **4b** can be recovered from reaction mixture even after several hours of reflux.

Table 3. Direct Azidation of Organic Substrates by Azidobenziodoxoles

entry	substrate	reaction conditions	product	yield (%)[a]
1	 **5a**	**2** (0.89 eq), CH_2Cl_2, reflux, 0.5 h	 **6a**	91%
2	**5a**	**4b** (0.91 eq), CH_2Cl_2, reflux, 3 h	**6a**	61%
3	 **5b**	**2** (0.91 eq), CH_2Cl_2, reflux, 0.5 h	 **6b**	77%
4	 **5c**	**2** (0.89 eq), CH_2Cl_2, reflux, 0.5 h	 **6c**	90%
5	 **7**	**2** (0.5 eq), $ClCH_2CH_2Cl$, reflux, 3 h benzoyl peroxide (cat.)	 **8**	76%
6	 **9**	**2** (0.5 eq), $ClCH_2CH_2Cl$, reflux, 3 h benzoyl peroxide (cat.)	 **10**	62%
7	 **12**	**2** (0.5 eq), $ClCH_2CH_2Cl$, reflux, 3 h benzoyl peroxide (cat.)	 **13**	51%
8	 **15**	**2** (1 eq), PhCl, 100-105 °C, 3-4 h benzoyl peroxide (cat.)	 **16**	68%
9	**15**	**4b** (1 eq), PhCl, 132 °C, 3 h benzoyl peroxide (cat.)	**16**	59%
10	 **17**	**2** (1 eq), PhCl, 100-105 °C, 3-4 h benzoyl peroxide (cat.)	 **18**	45%
11	**17**	**4b** (1 eq), PhCl, 132 °C, 3 h benzoyl peroxide (cat.)	**18**	62%
12	 **19**	**2** (1 eq), PhCl, 100-105 °C, 3-4 h benzoyl peroxide (cat.)	 **20**	45%
13	**19**	**4b** (1 eq), PhCl, 132 °C, 3 h benzoyl peroxide (cat.)	**20**	41%
14	 **21**	**2** (0.5 eq), $ClCH_2CH_2Cl$, reflux, 3 h benzoyl peroxide (cat.)	 **22**	23%
15	**21**	**4b** (1 eq), PhCl, 132 °C, 1 h benzoyl peroxide (cat.)	**22**	20%

[a] Isolated yields. [b] Additionally identified by reduction with $LiAlH_4$ to the respective amine **11**. [c] Additionally identified by reduction with $LiAlH_4$ to the respective amine **14**.

To demonstrate the general character of azidation of hydrocarbons, we studied reaction of azidoiodinanes **2,4b** with bicyclic and tricyclic hydrocarbons **9, 12, 15, 17,** and **19** (Table 3), all of which are known to be reactive in the free-radical hydrogen abstraction reactions.[16] The azidations were carried out in 1,2-dichloroethane or chlorobenzene at 83−132 °C in the presence of a catalytic amount of benzoyl peroxide. The

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process can be conveniently monitored by disappearance of the azide peak of the starting reagent at 2050 cm^{-1} and emergence of the product's peak at about 2090−2100 cm^{-1} in the IR spectrum of the reaction mixture. The reaction was generally complete in 3−4 h and, according to NMR and GC-MS data, the major products in each case were the respective azides **10, 13, 16, 18,** and **20** and 2-iodobenzoic acid. Pure azides can be isolated in good yield by column chromatography on silica gel. The best yields of azides **16, 18,** and **20** were obtained in chlorobenzene solution at temperatures 100−105 °C for reagent **2** and under reflux conditions (132 °C) for the less reactive azidoiodinane **4b**. Similar reactions of hydrocarbons with **2** generated from 2-iodosylbenzoic acid and $TMSN_3$ *in situ* usually gave lower yields of products. The presence of benzoyl peroxide is essential for the reaction; employment of a mixture azobis(isobutyronitrile)/benzoyl peroxide as radical initiator in some cases leads to a slight yield improvement.

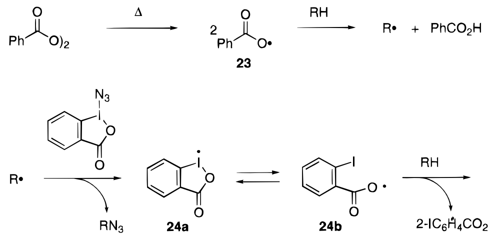
Reaction of *cis*-decalin **9** under these conditions selectively afforded tertiary azide **10** in good preparative yield. Product **10** was identified by its spectra and by reduction to the known amine **11**.[17]

Likewise, tricyclo[5.2.1.$0^{2,6}$]decane **12** was azidated with **2** at C-2 to give azide **13** as a yellow oil. For additional identification azide **13** was reduced to the respective amine **14** by treatment with $LiAlH_4$ in ether according to standard procedure.[3d] The structure of amine **14** was elucidated by comparison of its ^{1}H and ^{13}C NMR with the previously reported spectra of 2-substituted tricyclo[5.2.1.$0^{2,6}$]decanes.[16b,c]

Adamantane **15** is known to be reactive in the hydrogen abstraction reactions[16] because of the relatively high stability of the intermediate bridgehead free-radical.[18] However, it is generally less reactive than acyclic alkanes bearing tertiary hydrogens.[18] We found that azidations of adamantane **15** and 1,3-dimethyladamantane **17** required higher temperatures compared to hydrocarbons **7, 9,** and **12**. The best yield of 1-azidoadamantane **16** was obtained in the reaction of adamantane with reagent **2** at 100−105 °C using chlorobenzene as the solvent. Azidation of 1,3-dimethyladamantane **17** by reagent **2** under similar conditions afforded azide **18** in only 30−45% yield. However, the use of reagent **4b** instead of **2** and carrying out azidation at higher temperatures led to a substantial improvement of the product **18** yield. Azides **16** and **18** were isolated from the reaction mixture by column chromatography and identified by comparison of their spectra with the literature data.[19]

Norbornane **19** reacts with azidoiodinane **2** in the presence of a radical initiator to afford *exo*-2-azidonorbornane **20** as the principal product, without any detectable amounts of the alternative 1-azidonorbornane as the product of azidation at the bridgehead position. In a typical procedure, a mixture of azidoiodinane **2**, norbornane **19** (1−2 mol-equiv), and a catalytic amount of benzoyl peroxide is heated to 100−105 °C in a chlorobenzene solution. According to NMR spectra, the major components of the reaction mixture are *exo*-2-azidonorbornane **20**, 2-iodobenzoic acid, and unreacted norbornane. Pure 2-azidonorbornane was isolated from the reaction mixture by column chromatography and identified by comparison of ^{1}H NMR, ^{13}C NMR and IR spectra with the literature data.[20] Relatively low yields of 2-azidonorbornane (15−45%) are explained by a considerable decomposition of the starting reagent and the product at higher temperatures, required for the reaction. As a possible variation, iodinane **4b** can be used in this reaction as an azidating reagent, or reagent **2** can be generated *in situ* from the commercially available 2-iodosobenzoic acid and azidotrimethylsilane; however, the yields of **20** under these conditions are even lower. Formation of 2-azidonorbornane instead of the alternative 1-azidonorbornane is in agreement with the literature data on the predominant formation of *exo*-2-substituted products in radical substitution reactions of norbornane.[21]

Scheme 1



It should be emphaszied that these reactions of azidoiodinanes **2** and **4b** represent a first experimental procedure for the direct azidation of alkanes. Recently, azides of polycyclic bridgehead compounds have attracted an intense interest and research activity due to their high reactivity and some useful properties. For example, secondary azidonorbornenes are potentially important as energetic fuel additives,[22] and azidoadamantanes are used as precursors to various aza-bridged polycyclic systems.[19,23] To our knowledge, no direct preparation of azides from bridgehead hydrocarbons was reported in the literature. In particular, 2-azidonorbornane is usually synthesized by addition of HN_3 to norbornene,[20] while azidoadamantanes are prepared from the respective adamantanols or bromoadamantanes.[19]

The mechanism for azidation of alkanes with reagents **2** and **4b** clearly has a free-radical origin which is consistent with the literature data on radical mechanism for azidations by the unstable iodinanes, $PhI(N_3)_2$ and $PhI(N_3)OTMS$.[8c,9,24] However, in contrast with the previously reported reactions of the unstable iodinanes, azidations by azidobenziodoxoles **2** and **4b** require the presence of radical initiators and higher temperature. Specially performed experiments demonstrated that radical initiators did not catalyze decomposition of azidobenziodoxoles at 80−100 °C in the absence of the alkane. This result indicates that the presence of alkane is essential to initiate the radical chain process. A plausible mechanism for azidation of alkanes is shown in Scheme 1. The reaction is initiated by benzoyl radicals **23** generated by thermal decomposition of benzoyl peroxide. Radical **23** (or phenyl radical, product of its decarboxylation) can serve as the initial hydrogen abstractor from alkane. The propagation steps in this process involve the azide abstraction by alkyl radicals and the hydrogen abstraction by the 2-iodobenzoate radical **24**. In full agreement with this mechanistic scheme, the final isolated products are alkyl azide, RN_3, and 2-iodobenzoic acid.

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It is interesting to compare our results with the literature data on azidations by the unstable iodinanes, $PhI(N_3)_2$ and $PhI(N_3)OTMS$. Recently, Magnus and co-workers have found that the reaction of $PhIO/TMSN_3$ with cyclohexene and triisopropylsilyl enol ethers proceeds *via* an azido-radical addition process.[9b] In particular, cyclohexene reacts with $PhIO/TMSN_3$ at −45 °C in the presence of the stable radical TEMPO to afford a mixture of *cis*- and *trans*-1,2-diazidocyclohexanes in 80% yield. A plausible mechanism of this reaction involves the initial generation of azido-radicals from $PhI(N_3)_2$ and their subsequent addition to the double bond.[9b] In contrast with these data,[9b] azidobenziodoxoles **2,4** in the presence of TEMPO or benzoyl peroxide do not react with cyclohexene at temperatures below 0 °C, or at room temperature, even after several hours of stirring. The reaction of cyclohexene with reagent **2** proceeds only upon reflux in 1,2-dichloroethane (bp 83 °C) in the presence of catalytic amounts of benzoyl peroxide to afford the allylic azide **22** (Table 3) and 2-iodobenzoic acid as major products according to NMR spectra of the reaction mixture. No 1,2-diazidocyclohexane is formed under these conditions. The isolated yield of azide **22** is relatively low (23%) due to a substantial decomposition of the product under reaction conditions and during aqueous workup. Reagent **4b** reacts with cyclohexene only at higher temperature, upon reflux in chlorobenzene (bp 132 °C), to afford the respective azide **22** in a low preparative yield. These results are all consistent with the free radical chain mechanism shown in Scheme 1 and exclude the alternative pathway involving the azido-radicals as key intermediates.

Conclusions

In summary, we prepared first stable azidoiodinanes **2,4a** and **4b** from readily available benziodoxoles. The X-ray crystal structure establishes molecule **4b** as a five-membered iodine heterocycle with a weak covalent iodine-azide bond. The geometry of the $I^{(III)}NNN$ fragment in **4b** is similar to the literature electron diffraction data on monomeric iodine azide, IN_3, in gas phase.

The scope of azidations with compounds **2** and **4** demonstrate their usefulness as reagents for organic chemistry. It should be emphasized that their reactivity is generally different from the known reagent combinations $PhIO/TMSN_3$ or $PhI(OAc)_2/TMSN_3$, in which the unstable species $PhI(N_3)X$ or $PhI(N_3)_2$ serve as reactive intermediates in azidation reactions. In particular, the low stability of $PhI(N_3)X$ or $PhI(N_3)_2$ restricts its practical application only to low temperature reactions with the most reactive, nucleophilic organic substrates, such as alkenes, amines, and enol ethers, while stable azidoiodinanes **2** and **4b** can be applied even to hydrocarbons at higher temperatures. The mechanism of azidation of hydrocarbons with reagents **2** and **4** clearly has a free-radical origin which is indicated by the reaction conditions and the product composition.

Experimental Section

General Methods. All melting points were determined in an open capillary tube with a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer. NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz (^1H NMR) and 75 MHz (^{13}C NMR). Chemical shifts for ^1H and ^{13}C NMR are reported in parts per million (ppm). ^1H chemical shifts are referenced relative to the residual nondeuteriated solvent of chloroform at δ 7.24 or acetonitrile δ 1.93. The ^{13}C chemical shifts are referenced relative to $CDCl_3$ at δ 77.0 or CD_3CN δ 1.3. Mass spectra were obtained with a Hewlet-Packard 5970A GC-mass spectrometer (electron impact, 70 eV).

Microanalyses for stable products were carried out by Atlantic Microlab, Inc., Norcross, Georgia.

Materials. All commercial reagents were ACS reagent grade and used without further purification. 1-Hydroxy-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole **3a** was prepared from 2-iodobenzoic acid by a known method.[25] Benziodoxole **3b** was prepared by oxidation of 2-(2-iodophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol[26] with peracetic acid. Methylene chloride and acetonitrile were distilled from CaH_2 immediately prior to use. Other solvents were of commercial quality from freshly opened containers. The reaction flasks were flame-dried and flushed with nitrogen.

1-Azido-1,2-benziodoxole-3-(1*H*)-one (2). To a stirred mixture of 2-iodosobenzoic acid **3** (0.53 g, 2 mmol) in dry acetonitrile (20 mL) was added trimethylsilylazide (0.53 mL, 4 mmol) under nitrogen at room temperature. The reaction mixture was stirred for 10−15 h until the formation of a clear, pale yellow solution. The resulting solution was evaporated in vacuum to give slightly yellow microcrystalline residue of azide **2**, which was washed with anhydrous ether and dried in vacuum: yield 0.54 g (94%); mp 138−140 °C (dec; from CH_3CN); IR (CCl_4) 3065 (Ar), 2048 (N_3), 1643 (C=O) cm^{-1}; ^1H NMR ($CDCl_3/CF_3COOH$, 20:1) δ 8.32 (d, 1H, $J = 8$ Hz), 8.05 (m, 2H, $J = 8$ Hz), 7.85 (t, 1H, $J = 8$ Hz); ^{13}C NMR ($CDCl_3/CF_3COOH$, 20:1) δ 171.11 (C=O), 137.28, 128.69, 126.69, 126.57, 118.84, 117.66 (Ar). Anal. Calcd for $C_7H_4IO_2N_3$: C, 29.09; H, 1.39. Found: C, 29.40; H, 1.48.

CAUTION: Azidoiodinane **2** decomposes with an explosion upon heating to 130−140 °C and should be handled with care.

1-Azido-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (4a). To a stirred solution of 1-hydroxy-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole **3a** (0.200 g, 0.72 mmol) in dry CH_3CN (15 ml) was added azidotrimethylsilane (0.144 mL, 1.09 mmol) under nitrogen at room temperature. After stirring 2 h reaction mixture was cooled to −15 °C, and the resulting yellow precipitate of **4a** was filtered under nitrogen and dried in vacuum: yield 0.189 g (87%); mp 114−117 °C (from CH_3CN); IR (CCl_4) 2977 (Ar), 2921, 2034 (N_3), 1558, 1458, 1435, 1241, 1154, 1110, 1002, 948 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78 (m, 1H), 7.55 (m, 2H), 7.26 (m, 1H), 1.53 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 149.12, 130.78, 130.17, 127.70, 126.60, 113.91 (Ar), 83.03 ($C(CH_3)_2$), 29.44 ($C(CH_3)_2$). Anal. Calcd for $C_9H_{10}ION_3$: C, 35.66; H, 3.33; N, 13.86. Found: C, 35.73; H, 3.31; N, 13.96.

1-Azido-3,3-bis(trifluoromethyl)-3-(1*H*)-1,2-benziodoxole (4b). To a stirred mixture of 1-hydroxy-3,3-bis(trifluoromethyl)-3-(1*H*)-1,2-benziodoxole **3b** (0.5 g, 1.3 mmol) in dry CH_3CN (20 mL) was added trimethylsilylazide (0.35 mL, 2.6 mmol) under nitrogen at room temperature. The reaction mixture was stirred for 18 h, and then the resulting yellow solution was evaporated in vacuum to give a pale yellow microcrystalline residue of azide **4b**: yield 0.49 g (92%); mp 147−150 °C (from CH_3CN); IR (KBr) 3082 (Ar), 2046 (N_3), 1266, 1186, 1141, 1111, 1041 (CF_3) cm^{-1}; ^1H NMR ($CDCl_3/CD_3CN$, 10:1) δ 7.9−7.65 (m, C_6H_4); ^{13}C NMR ($CDCl_3/CD_3CN$, 10:1) δ 134.04, 131.79, 131.48, 130.33, 128.30 (Ar), 123.42 (q, J = 290 Hz, $C(CF_3)_2$), 114.26, 84.40 (septet, $J = 30.5$ Hz, $C(CF_3)_2$). Anal. Calcd for $C_9H_4IF_6ON_3$: C, 26.30; H, 0.98. Found: C, 27.04; H, 1.14. X-ray quality single crystals were obtained by slowly evaporating a solution of **4b** in CH_3CN in an open air container.

Crystallographic Data for 4b. Empirical formula: $C_9H_4F_6IN_30$, $M = 411.046$, monoclinic, space group $P2_1/n$ (no. 14); cell constants $a = 11.850$ (3) Å, $b = 6.993$ (2) Å, $c = 15.188$ (2) Å, $\beta = 99.61$ (2) deg, $V = 1240.79$ Å^3, $Z = 4.0$, $D_c = 2.200$ g·cm^{-3}. Crystal dimensions 0.21 × 0.20 × 0.16 mm. Data were collected at 291 K on an Enraf-Nonius CAD-4 diffractometer, MoKα radiation, $\lambda = 0.71073$ Å. The intensities of 2497 nonzero reflections were measured; 2183 of unique reflections in the range $4.0 < 2\Theta < 50.0°$ were used for the structure analysis (scan technique $\Theta/2\Theta$, scan width $0.800 + 0.340(\tan \Theta)$ deg, data collection position: bisecting with $\omega = 0$). No decay correction was applied [absorption correction, empirical; minimum % transmission, 76.31; maximum % transmission, 99.96; average % transmission, 88.81; highest peak in final difference Fourier 1.138 e/Å^3; summary of final least squares refinement: weighting scheme−non-Poisson contribution;

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ignorance factor, $P = 0.05$; data rejected if $I < 3.00\ \sigma(I)$ and $\sin \Theta/\lambda < 0.0500$; 1943 observations; 172 variables; data-to-parameter ratio 10.06; shift to error ratio 0.004; error in an observation of unit weight 1.9166; *R* factor 0.0363; weighted *R* factor 0.0484]. All hydrogen atoms were calculated and included in the final least-squares refinements. All calculations were carried out using the MOLEN software distributed by Enraf-Nonius.

Typical Procedure for Azidation of *N*,*N*-Dimethylarylamines with Azidobenziodoxole 2. To a stirred mixture of azidobenziodoxole **2** (0.075 g, 0.26 mmol) in dry dichloromethane (10 mL) was added 4-bromo-(*N*,*N*-dimethylaniline) (0.057 g, 0.29 mmol) under nitrogen at room temperature. The reaction mixture was then refluxed for 0.5 h. The reaction can be monitored by disappearance of the azide peak of the starting reagent at 2048 cm^{-1} and emergence of the product's peak at about 2100 cm^{-1} in the IR spectrum of the mixture. According to NMR spectra, 4-bromo-(*N*-azidomethyl-*N*-methyl)aniline **6a** and 2-iodobenzoic acid were the only reaction products. Pure **6a** can be isolated by column chromatography on silica gel: yield 0.115 g (91%); IR (neat) 2102 (N_3) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.0 (m, 5H, Ph), 4.84 (s, 2H, CH_2); 3.09 (s, 3H, CH_3); MS (EI, 70 eV) *m*/*z* (%) 146 (100), M^+. Products **6b,c** were prepared similarly and identified by comparison of their IR and NMR spectra with the literature data.[9c]

***N*-Azidomethyl-*N*-methylaniline (6b).** According to the above typical procedure, **2** (0.235 g, 0.813 mmol) was reacted with *N*,*N*-dimethylaniline (0.108 g, 0.894 mmol) to give 0.101 g (77%) of **6b**: IR (neat) 2098 (N_3, s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.0 (m, 5H, Ph), 4.83 (s, 2H, CH_2), 3.05 (s, 3H, CH_3); *m*/*z* (%) 162 (100), M^+.

4-(*N*-Azidomethyl-*N*-methylamino)pyridine (6c). By following the above typical procedure, reaction of **2** (0.307 g, 1.064 mmol) and 4-dimethylaminopyridine (0.134 g, 1.17 mmol) gave 0.156 g (90%) of **6c**: IR (neat) 2106 (N_3, s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.5 (m, 2H), 7.87 (dd, 2H) 4.91 (s, 2H, CH_2), 3.24 (s, 3H, CH_3).

Azidation of 4-Bromo-*N*,*N*-dimethylaniline with Azidobenziodoxole 4b. According to the above typical procedure, reagent **4b** (0.212 g, 0.516 mmol) was reacted with 4-bromo-(*N*,*N*-dimethylaniline) (0.114 g, 0.567 mmol) in dichloromethane (10 mL) at reflux for 3 h to give the respective azide **6a** as the major product: isolated yield 0.076 g (61%).

2-Azido-2,4,4-trimethylpentane (8). Typical Procedure. To a stirred mixture of azidobenziodoxole **2** (0.234 g, 0.81 mmol) in dry 1,2-dichloroethane (15 mL) was added 2,2,4-trimethylpentane **7** (0.267 mL, 1.62 mmol). Catalytic amounts of benzoyl peroxide (0.005 g) and 1,1′-azobis(cyclohexanecarbonitrile) (0.005 g) were added as radical initiators. The reaction mixture was then refluxed for 3 h. The resulting solution was evaporated in vacuum. A brownish residue was dissolved in hexane (20 mL) and filtered through a silica gel plug to give a colorless solution. It was washed with 10% NaOH (2 × 30 mL) and water (30 mL), dried over Na_2SO_4, and evaporated in vacuum to give the resulting azide **8** as a colorless oil: yield 0.095 g (76%); IR (neat) 2099 (N_3) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 2H, CH_2), 1.32 (s, 6H, $C(CH_3)_2$), 1.02 (s, 9H, $C(CH_3)_3$); lit. data for 2-azido-2,4,4-trimethylpentane: IR (neat) $\nu = 2100$ (N_3); ^{1}H NMR $\delta = 1.52$ (s, 2H), 1.31 (s, 6H), 1.02 (s, 9H).[27]

9-Azido(decahydronaphthalene) (10). By following the above typical procedure, reaction of **2** (0.305 g, 1.055 mmol) and *cis*-decahydronaphthalene **9** (0.292 g, 2.110 mmol) gave 0.117 g (62%) of **10** as a yellow oil: IR (neat) 2093 (N_3, s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75−1.9 (m); MS (EI, 70 eV) *m*/*z* (%) 179 (100), M^+. Treatment of azide **10** with an excess of $LiAlH_4$ in ether at room temperature according to standard procedure[3d] afforded the respective, known amine **11**.[17]

2-Azidotricyclo[5.2.1.0^{2,6}]decane (13). According to the above typical procedure, **2** (0.330 g, 1.142 mmol) was reacted with tricyclo[5.2.1.0^{2,6}]decane **12** to give the respective azide **13** as a yellow oil: yield 0.103 g (51%); IR (neat) 2090 (N_3) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2−2.5 (m).

For additional identification azide **13** was reduced to amine **14** by treatment with $LiAlH_4$ in ether according to standard procedure.[3d] For amine **14**: a colorless oil; IR (neat) 3355, 3276 (NH_2, s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1−2.2 (m); ^{13}C NMR ($CDCl_3$) δ 69.0, 56.67, 49.85, 41.65, 40.93, 36.88, 28.74, 26.41, 21.62; *m*/*z* (%) 151 (100), M^+. Anal. for **14·HCl**: Calcd for $C_{10}H_{18}ClN$: C, 63.99; H, 9.67; N, 7.46. Found: C, 63.94; H 9.45; N, 7.17. ^{1}H and ^{13}C NMR of **14** are in good agreement with previously reported spectra of 2-substituted tricyclo[5.2.1.0^{2,6}]decanes.[16b,c]

Typical Experimental Procedure for the Azidation of Bridgehead Hydrocarbons (15, 17, and 19) with Azidoiodinane 2. To a stirred mixture of azidobenziodoxole **2** (0.14 g, 0.48 mmol) and adamantane **15** (0.07 g, 0.47 mmol) in dry chlorobenzene (20 mL) was added a catalytic amount of benzoyl peroxide (5 mg) under nitrogen at room temperature. The reaction mixture was then stirred at 100−105 °C for 3−4 h, and the resulting dark orange solution was evaporated in vacuum to give a residual brown oil which was passed through a short silica gel column with hexane to give 1-azidoadamantane **16** as a clear, partially crystalline oil: R_f (hexane) = 0.72, yield 0.057 g (68%); mp 77−80 °C (from CH_3OH) (lit.[19a] mp 76−77 °C).

1-Azido-3,5-dimethyladamantane **18** and *exo*-2-azidonorbornane **20** were prepared similarly. For **18**: 45% yield; colorless oil; IR (neat) 2911, 2844, 2089 (N_3), 1450, 1283, 1017, cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 2.2$ (1H, m, CH), 1.1−2.0 (12H, m, 6CH_2), 0.87 (6H, s, 2Me); lit. data for **18** mp 25−26 °C;[19a] IR (KBr) 2100 (N_3); ^{1}H NMR ($CDCl_3$) $\delta = 2.0$−2.4 (m, 2H), 1.0−1.8 (m, 12H), 0.89 (s, 6H).[19b] For **20**: 45% yield; colorless oil; IR (neat): 2950, 2090 (N_3), 1450, 1290, 1001, cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 3.45$ (1H, dd, J = 7.5 and 2.5 Hz, CHN_3), 2.28 (2H, m, 2CH), 1.1−1.7 (8H, m); ^{13}C NMR ($CDCl_3$) $\delta = 64.0$ (d), 41.6 (d), 38.2 (d), 35.5 (t), 34.7 (t), 28.1 (t), 25.5 (t). MS (EI, 70 eV) *m*/*z* (%) 137 (5), M^+; lit. data[20] for *exo*-2-azidonorbornane IR (neat) 2090 (N_3); ^{1}H NMR $\delta = 3.45$ (1H, ddd, *J* = 7.6, 2.6, and 1.3 Hz, CH), 2.28 (2H, s, CH), 1.1 (3H, m), 1.5 (5H, m).

Reactions of Azidoiodinanes with Cyclohexene. To a stirred mixture of azidobenziodoxole **2** (0.325 g, 1.125 mmol) in dry 1,2-dichloroethane (15 ml) was added cyclohexene (0.23 mL, 2.25 mmol) at room temperature under nitrogen. Catalytic amounts of benzoyl peroxide (0.005 g) and 1,1′-azobis(cyclohexanecarbonitrile) (0.005 g) were added as radical initiators. The reaction mixture was then refluxed for 3 h. The resulting solution was evaporated in vacuum. A yellow oil was dissolved in hexane (20 mL) and filtered through a silica gel plug to give a colorless solution. It was washed with 10% NaOH (2 × 30 mL) and water (30 mL), dried over Na_2SO_4 and evaporated in vacuum to give the resulting azide **22** as a colorless oil: yield 0.032 g (23%); IR (neat) 2095 (N_3,s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.3−6.0 (m, 2H), 3.7−4.1 (m, 1H), 1.3−2.3 (m, 6H); MS (EI, 70 eV) *m*/*z* (%) 123 (100), M^+; lit. data[28] for 3-azido-1-cyclohexene IR (neat) 2095 (N_3, s) cm^{-1}; ^{1}H NMR (CCl_4) δ 5.43−6.15 (m, 2H), 3.58−4.40 (m, 1H), 1.5−2.4 (m, 6H).

Likewise, azidobenziodoxole **4b** (0.247 g, 0.601 mmol) was reacted with cyclohexene (0.122 mL, 1.202 mmol) in chlorobenzene (10 mL) at reflux (132 °C) for 1 h to give the respective azide **22** as the major product; isolated yield 0.015 g (20%).

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Supporting Information Available: Tables of positional parameters and ESD, anisotropic displacement parameters, and bond lengths and bond angles for compound **4b** (9 pages). Ordering information is given on any current masthead page.

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