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Synthesis and Structure of Hypervalent Diacetoxybromobenzene and Aziridination of Olefins with Imino-λ^3-bromane Generated in Situ under Metal-Free Conditions

Md. Mahbubul Hoque,[†] Kazunori Miyamoto,[†] Norihiro Tada,[†] Motoo Shiro,[‡] and Masahito Ochiai*,[†]

Graduate School of Pharmaceutical Sciences, University of Tokushima, 1-78 Shomachi, Tokushima 770-8505, Japan, and Rigaku Corporation, 3-9-12 Matsubara, Akishima, Tokyo 196-8666, Japan

mochiai@ph.tokushima-u.ac.jp

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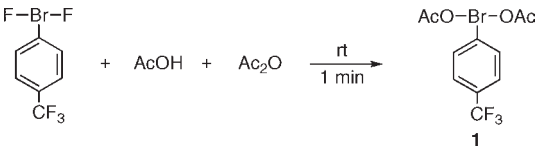
ABSTRACT

Ligand exchange of *p*-$CF_3C_6H_4BrF_2$ with acetoxy groups using AcOH and Ac_2O affords (diacetoxybromo)benzene in a high yield, which undergoes aziridination of alkenes in the presence of $TfNH_2$ and sulfamate esters in one pot under mild conditions. The aziridination with $TfNH_2$ proceeds stereospecifically with retention of stereochemistry of olefins at room temperature using limiting amounts of olefins under transition-metal-free conditions. The one-pot aziridination procedure using sulfamate esters can be applied to the intramolecular versions.

(Diacetoxyiodo)benzene $PhI(OAc)_2$ is among the most popular and valuable oxidizing agents in a hypervalent organo-λ^3-iodane family.[1] The commercially available diacetoxy-λ^3-iodane has enjoyed widespread application as a powerful oxidant because of its environmentally friendly nature and oxidizes a wide range of functionalities including alkenes, alkynes, alcohols, phenols, amines, sulfides, and carbonyl compounds under mild conditions. On the other hand, the chemistry of the nearest neighbors, (diacetoxybromo)arenes, remains to be established.[2] We report herein, for the first time, the synthesis and characterization of diacetoxy(aryl)-λ^3-bromane (**1**) (Scheme 1). Diacetoxy-λ^3-bromane (**1**) undergoes aziridination of alkenes in the presence of trifluoromethanesulfonamide ($TfNH_2$). The aziridination proceeds stereospecifically at room temperature using limiting amounts of alkenes under transition metal-free conditions and probably involves in situ generation of *N*-triflylimino-λ^3-bromane (**2**) as an active nitrenoid species.

Scheme 1



Double ligand exchange of fluorine atoms of Frohn reagent *p*-trifluoromethylphenyl(difluoro)-λ^3-bromane[3] with acetoxy groups takes place rapidly at room

[†] Tokushima University.
[‡] Rigaku Corporation.

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temperature: thus, mixing the difluoro-λ^3-bromane with 2.2 equiv each of acetic acid and acetic anhydride in a Teflon PFA vessel for 1 min under argon produced, after removal of volatile materials liberated in vacuo, crystalline *p*-trifluoromethyl(diacetoxybromo)benzene (**1**) in 90% yield. Acetic anhydride probably traps hydrogen fluoride generated in situ during the ligand exchange reaction, via the formation of acetyl fluoride.[4] Use of trimethylsilyl acetate, instead of acetic anhydride, also afforded diacetoxy-λ^3-bromane **1** (83%). Diacetoxybromane **1** is rather air sensitive but can be kept at room temperature under argon in a PFA tube for more than 2 months without any decomposition. The ^{1}H NMR spectrum in $CDCl_3$ showed a set of characteristic signals assigned to the disubstituted phenyl group [δ 8.07 (*o*) and 7.81 (*m*) ppm] (see Figure S1(A), Supporting Information). The ^{13}C resonance of the *ipso* carbon atom appeared at δ 142.0 ppm. The polarized hypervalent $O^{\delta-}\cdots Br^{\delta+}\cdots O^{\delta-}$ bond tends to weaken the C=O double bond, and hence, bromane **1** shows a lower IR absorption by ca. 100 cm^{-1} at 1684 cm^{-1} compared to acetyl hypobromite (Figure S1(C), Supporting Information).[5]

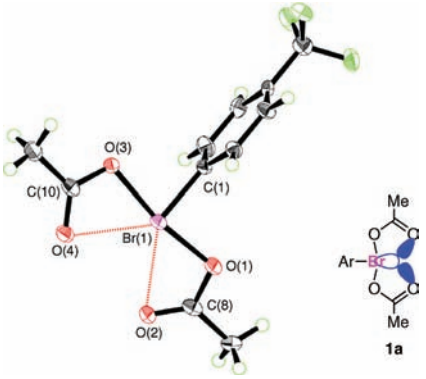

Figure 1. ORTEP drawing of diacetoxy-λ^3-bromane **1** with thermal ellipsoids at 50% probability and three-center secondary bonding model **1a**. Selected bond lengths (Å) and angles (deg): Br1−C1 1.914(5), Br1−O1 2.009(4), Br1−O3 2.064(3), Br1···O2 2.796(2), Br1···O4 2.785(4), C1−Br1−O1 85.56(16), C1−Br1−O3 84.85(16), O1−Br1−O3 170.31(14).

Recrystallization from pentane−dichloromethane at −78 °C afforded single crystals (colorless prisms) that were suitable for X-ray crystallography (Figure 1). Diacetoxy-λ^3-bromane **1** essentially exhibits a T-shaped geometry with the two acetoxy groups occupying apical positions and is regarded as pentagonal planar arrangement with two additional intramolecular close contacts around the bromane(III) atom, which is reminiscent of the structure of (diacetoxyiodo)benzene.[6,7] The rms deviation of the six atoms (Br1, C1, and O1−O4) from the least-squares plane is 0.282(1) Å, and the sum of the bromine centered bond angles is $\Sigma°Br = 365.08°$. The plane of the benzene ring makes a dihedral angle of 74.89° with this plane. The Br1···O2 and Br1···O4 distances are considerably longer than the computed covalent single bond length of 1.80 Å but definitively shorter than the sums of the van der Waals radii of Br (1.85 Å) and O (1.52 Å).[8] Cooperative donation of the two lone pairs of electrons of the carbonyl oxygen atoms to the vacant Br1−C1 σ^* orbital as shown in three-center bonding model **1a**, originally proposed by Alcock,[6] will be responsible for these secondary Br···O contacts. The C1−Br1−O1 and C1−Br1−O3 bond angles are considerably greater than those (81.4° and 82.6°) for PhI(OAc)$_2$,[6] probably because of the increased nonbonded repulsions between the substituents on bromane(III) with a decreased atomic size.

Aryl(sulfonylimino)-λ^3-iodanes serve as excellent nitrenoid progenitors in the aziridination of alkenes and in the C−H amidation of alkanes in the presence of transition-metal catalysts, where use of a metal catalyst (Cu, Rh, Mn, Ru, or Ag) is crucial to the success of these nitrenoid transfers to generate active metal-imido species.[9,10] Recently, we reported the synthesis of *N*-triflylimino-λ^3-bromane **2**, which involves a facile ligand exchange of Frohn reagent with triflylamide in acetonitrile.[11] Triflylimino-λ^3-bromane **2** directly transfers the imino group to olefins and heteroatom nucleophiles involving nitrogen heterocycles, sulfur compounds, and iodoarenes at room temperature under metal-free conditions.[11,12] Highly regioselective amination of unactivated aliphatic C−H bonds also proceeds smoothly by just mixing **2** with alkane without thermal activation.[13,14] These results are in marked contrast to the reactions of sulfonylimino-λ^3-iodanes, which requires

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(9) For reviews of aryl(sulfonylimino)-λ^3-iodanes, see: (a) Collet, F.; Dodd, R. H.; Dauban, P. *Chem. Commun.* **2009**, 5061. (b) Diaz-Requejo, M. M.; Perez, P. J. *Chem. Rev.* **2008**, *108*, 3379. (c) Halfen, J. A. *Curr. Org. Chem.* **2005**, *9*, 657. (d) Du Bois, J. *Chemtracts: Org. Chem.* **2005**, *18*, 1. (e) Dauban, P.; Dodd, R. H. *Synlett* **2003**, 1571. (f) Muller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905.

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(14) For a review of triflylimino-λ^3-bromane **2**, see: Ochiai, M.; Miyamoto, K.; Hayashi, S.; Nakanishi, W. *Chem. Commun.* **2010**, *46*, 511.

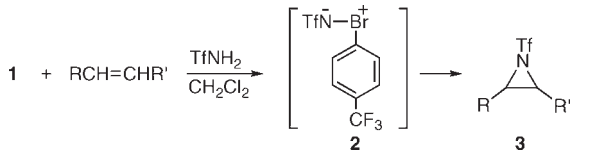
activation by a metal catalyst, and indicate that the λ^3-bromane **2** itself functions as a reactive organo nitrenoid at room temperature without any transition metal activation. *N*-Triflylimino-λ^3-bromane **2**, however, is thermally labile and rather sensitive to atmospheric moisture, and should be kept in a refrigerator under argon. In order to avoid some difficulties associated with the long period of storage and to enhance the synthetic value of these nitrenoid transfer reactions, development of the methods for the in situ generation of imino-λ^3-bromane **2** seems to be highly desirable.[15]

Initial attempts for one-pot aziridination of (*Z*)-4-octene using a combination of Frohn reagent and triflylamide were found to be fruitless, because of the modest yields of *N*-triflylaziridine **3g** and of the lack of reproducibility (Scheme S1, Supporting Information): thus, yields of *N*-triflylaziridine **3g** changed irregularly from 11% to 53%. Reliable and efficient aziridination method of olefins using triflylamide was developed by changing Frohn reagent to diacetoxy(aryl)-λ^3-bromane **1** under mild conditions without using a metal catalyst. Representative results are summarized in Table 1. Premixing of each 1.2 equiv of diacetoxy-λ^3-bromane **1** and triflylamide in dichloromethane at 0 °C for 10 min and the subsequent addition of (*Z*)-4-octene (method A) produced a high yield (84%) of *cis*-aziridine **3g** stereoselectively (Table 1, entry 9). Initial formation of *N*-triflylimino-λ^3-bromane **2** under the conditions was suggested by its isolation in a high yield in a separate experiment (Scheme S2, Supporting Information). Very interestingly, addition of diacetoxy-λ^3-bromane **1** to a solution of triflylamide and (*Z*)-4-octene in dichloromethane (method B) also gave rise to *cis*-**3g** in a high yield (entry 10). This result indicates that premixing of diacetoxybromane **1** with triflylamide, i.e., preformation of imino-λ^3-bromane **2**, is not essential for our one-pot aziridination of olefin and that the rate of reaction of λ^3-bromane **1** with triflylamide will be considerably greater than that with (*Z*)-4-octene.[16]

The results shown in Table 1 are comparable to those obtained by the use of triflylimino-λ^3-bromane **2** with keeping the following scenario:[11] (1) High yields of aziridines **3** were produced using limiting amounts of starting olefins, in contrast to most of the reported reactions with preformed imino-λ^3-iodanes, which rely on excess amounts of substrate (3 or more equivalents) to effect high product conversion.[10] (2) The aziridination was exclusively stereospecific with retention of stereochemistry of both *Z*- and *E*-olefins, which is a relatively rare example of stereochemical retention in the aziridinations.[9c] (3) The rates of aziridination of *cis*-1,2-disubstituted olefins were larger compared to those of *trans* isomers. (4) The reaction proceeded smoothly at 0 °C or at ambient temperature under transition metal-free conditions. (5) No formation of any allylic C−H amidation side product was detected.[10a,17]

Reductive cleavage of triflylamides, yielding parent amines, seems to be a difficult process;[18] however, use of Red-Al under mild reaction conditions was found to be an

Table 1. One-Pot Aziridination of Olefins with in Situ Generated Imino-λ^3-bromane **2** Using $TfNH_2$[a]



2 **3**

entry	olefin	method[b]	temp (°C)	time (h)	product yield[c] (%)
1	cyclohexene	A	0	3	**3a** 72 (80)
2	cyclohexene	B	0	3	**3a** 70 (78)
3	cycloheptene	A	0	2	**3b** 88 (98)
4	*cis*-cyclooctene	A	0	1	**3c** 84 (96)
5	*cis*-cyclooctene	B	0	1	**3c** 80 (92)
6	norbornene	A	0	4	**3d** 66 (73)
7	$Me_2C{=}CMe_2$	A	0	1	**3e** 3 (89)
8[d]	n-$C_8H_{17}CH{=}CH_2$	A	25	7	**3f** 73 (75)
9	*Z*-PrCH=CHPr	A	0	3	**3g** 84 (97)
10	*Z*-PrCH=CHPr	B	0	3	**3g** 87 (98)
11[d]	*E*-PrCH=CHPr	A	25	6	**3h** 73 (80)
12	*Z*-PhCH=CHMe	A	0	1	**3i** 84 (91)
13	*E*-PhCH=CHMe	A	25	8	**3j** -[e]
14	*Z*-PhCH=CHPh	A	0	3.5	**3k** 79 (78)
15	*E*-PhCH=CHPh	A	25	2.5	**3l** -
16	$PhCH{=}CH_2$	A	0	9	**3m** 78 (86)
17	p-$ClC_6H_4CH{=}CH_2$	A	0	24	**3n** 80
18	p-$CF_3C_6H_4CH{=}CH_2$	A	0	30	**3o** 66 (70)

[a] Conditions: 1:1.2:1.2 olefin/$TfNH_2$/diacetoxy-λ^3-bromane **1**, dichloromethane, Ar. [b] For details of methods A and B, see text and Supporting Information. [c] Isolated yields. Numbers in parentheses are ^{1}H NMR yields. [d] 2 equiv of bromane **1** and $TfNH_2$ were used. [e] 1-Acetoxy-2-(triflylamino)-1-phenylpropane (*syn*/*anti* = 71:29) was isolated in 45% yield.

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(16) Oxidations of olefins with aryl-λ^3-iodanes have been studied extensively.[1] For the reaction of olefins with trifluoro-λ^3-bromane BrF_3, see: (a) Hagooly, A.; Rozen, S. *Chem. Commun.* **2004**, 594. (b) Rozen, S. *Acc. Chem. Res.* **2005**, *38*, 803.

(17) For transition-metal-catalyzed allylic C−H amidations using imino-λ^3-iodanes, see: (a) Liang, C.; Collet, F.; Robert-Peillard, F.; Muller, P.; Dodd, R. H.; Dauban, P. *J. Am. Chem. Soc.* **2008**, *130*, 343. (b) Xu, Q.; Appella, D. H. *Org. Lett.* **2008**, *10*, 1497. (c) Guthikonda, K.; Wehn, P. M.; Caliando, B. J.; Du Bois, J. *Tetrahedron* **2006**, *62*, 11331. (d) Caselli, A.; Gallo, E.; Ragaini, F.; Oppezzo, A.; Cenini, S. *J. Organomet. Chem.* **2005**, *690*, 2142. (e) Kohmura, Y.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 3339. (f) Au, S.-M.; Zhang, S.-B.; Fung, W.-H.; Yu, W.-Y.; Che, C.-M.; Cheung, K.-K. *Chem. Commun.* **1998**, 2677. (g) Mahy, J. P.; Bedi, G.; Battioni, P.; Mansuy, D. *Tetrahedron Lett.* **1988**, *29*, 1927.

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efficient method for the reductive deprotection of *N*-triflylaziridines. For instance, treatment of *cis*-diphenylaziridine **3k** with sodium bis(2-methoxyethoxy)aluminum dihydride (10 equiv) in toluene at 0 °C for 3 h under argon afforded the corresponding amine in a high yield (82%), without formation of ring-opened byproduct (Scheme 2). In this deprotection, isomerization to *trans*-2,3-diphenylaziridine was not detected.

Scheme 2

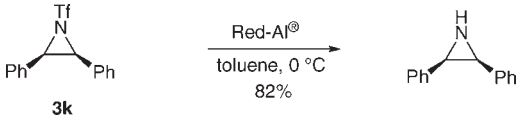
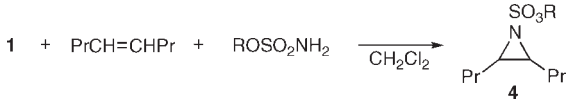


Table 2. Aziridination of 4-Octene with Sulfamate Esters[a]



					product	
entry	olefin	$ROSO_2NH_2$	temp (°C)	time (h)	yield[b] (%)	ratio[c]
1	*Z*	$CCl_3CH_2OSO_2NH_2$	0	5	**4a** 77 (81)	83:17
2	*E*	$CCl_3CH_2OSO_2NH_2$	25	3	**4a** 62 (71)	26:74
3	*Z*	$CF_3CH_2OSO_2NH_2$	0	8	**4b** 76 (88)	82:18
4	*E*	$CF_3CH_2OSO_2NH_2$	25	3	**4b** 75 (90)	30:70
5	*Z*	$EtOSO_2NH_2$	0	2	**4c** 78 (84)	43:57
6	*E*	$EtOSO_2NH_2$	25	4	**4c** 73(100)	27:73

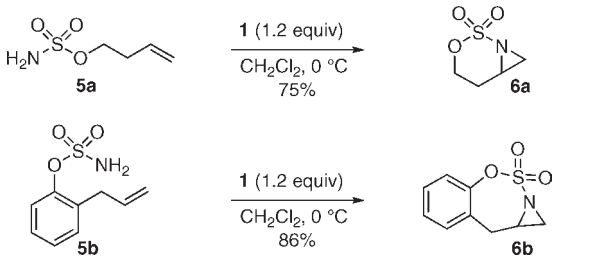
[a] Conditions: method B, 1:1.2:1.2 4-octene/$ROSO_2NH_2$/diacetoxy-λ^3-bromane **1**, dichloromethane, Ar. [b] Isolated yields. Numbers in parentheses are ^{1}H NMR yields. [c] *Cis*/*trans* ratios of **4** determined by ^{1}H NMR of crude reaction mixtures.

Instead of triflylamide, use of other amides such as *p*-nitro-, 2,4-dinitro-, and 3,5-bis(trifluoromethyl)-benzenesulfonamides[19] and methanesulfonamide showed no evidence for formation of aziridines under the conditions of method A and B; however, the bromane(III)-induced aziridination of double bonds in the absence of transition metal catalysts can be extended to the reaction of alkoxysulfonamides (sulfamates).[10d,20] Thus, method B resulted in the good yield formation of aziridines **4** by the reaction of trichloro-, trifluoro-, or unsubstituted ethyl sulfamate with a limiting amount of (*Z*)- and (*E*)-4-octene (Table 2). In these sulfamate-transfer reactions, however, loss of stereochemistry of olefins was detected to a great extent, especially in the reaction of ethyl sulfamate with (*Z*)-octene (Table 2, entry 5), which is in marked contrast to the reactions of triflylamide (Table 1). Formation of *N*-(alkoxysulfonyl)-imino-λ^3-bromane species is assumed to be involved in the *N*-atom transfer process; however, we could not detect their intermediacy by ^{1}H NMR tube experiments (Scheme S3, Supporting Information). Alkoxysulfonyl moieties serve as convenient amine protecting groups and alkoxysulfonylated aziridines are known to be effective substrates in ring-opening reactions with *S*-, *N*-, and *O*-centered nucleophiles.[10d]

The one-pot aziridination procedure using sulfamate esters can be applied to the intramolecular versions (Scheme 3): thus, olefinic sulfamate esters **5a** and **5b** by the reaction with diacetoxy-λ^3-bromane **1** under our conditions afforded bicyclic **6a**[10d,20b] and tricyclic aziridine **6b**[21] in good yields.

Thus, a hitherto unknown kind of diacetoxy(aryl)-λ^3-bromane was synthesized and well characterized. The λ^3-bromane makes it possible to undergo aziridinations of alkenes with triflylamide and sulfamate esters in one-pot under transition metal-free, mild conditions. The aziridination method probably relies on in situ generation of active *N*-sulfonylimino-λ^3-bromanes as well as the vastly enhanced hypernucleofugality of aryl-λ^3-bromanyl groups compared to that of aryl-λ^3-iodanyl groups.[22] Oxidation reactions of other functional groups such as carbonyl compounds and amides with diacetoxy-λ^3-bromane **1** are under active investigation.

Scheme 3



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Supporting Information Available. Experimental procedures, Figure S1, Schemes S1–S3, and X-ray crystallographic data for **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

(19) We supposed that these arenesulfonamides with electron-withdrawing substituents might condense with diacetoxybromane **1** to produce imino-λ^3-bromane because they do not undergo λ^3-bromane-induced Hofmann rearrangement. See: Ochiai, M.; Okada, T.; Tada, N.; Yoshimura, A.; Miyamoto, K.; Shiro, M. *J. Am. Chem. Soc.* **2009**, *131*, 8392.

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