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Benchtop-Stable Hypervalent Bromine(III) Compounds: Versatile Strategy and Platform for Air- and Moisture-Stable λ^3 -Bromanes

Kazunori Miyamoto,^{*,||} Motomichi Saito,^{||} Shunsuke Tsuji, Taisei Takagi, Motoo Shiro, Masanobu Uchiyama,^{*} and Masahito Ochiai^{*}

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ABSTRACT: We present the first synthesis of air/moisture-stable λ^3 -bromanes (9 and 10) by using a cyclic 1,2-benzbromoxol-3one (BBX) strategy. X-ray crystallography and NMR and IR spectroscopy of N-triflylimino- λ^3 -bromane (12) revealed that the bromine(III) center is effectively stabilized by intramolecular R–Br–O hypervalent bonding. This strategy enables the synthesis of a variety of air-, moisture-, and benchtop-stable Br-hydroxy, -acetoxy, -alkynyl, -aryl, and bis[(trifluoromethyl)sulfonyl]methylide λ^3 bromane derivatives.

• he invention of new chemical reagents is a fertile area of research in synthetic chemistry, providing novel strategies for efficient synthetic access to compounds of commercial and academic importance. For example, hypervalent iodine(III) reagents (denoted here as λ^3 -iodanes) are an important class of organic reagents, serving as unique electrophiles/oxidants that are employed extensively in academia and industry.¹⁻³ In contrast, the chemistry of λ^3 -bromanes has been little investigated, mainly due to the lack of efficient, user-friendly preparation methods.4,5 Much of the challenge involved in preparing λ^3 -bromanes resides in the innate thermodynamic barrier to oxidation of Br(I) arising from its great electronegativity (Br: 2.96 > I: 2.66),⁶ as well as its large ionization (IP) potential [e.g., PhBr (IP: 8.98 eV) > PhI (IP: 8.69 eV).⁷³ The first synthesis of the Br(III) analogue, λ^3 -bromane, by Sandin and Hay dates back to 1952.9 They elegantly overcame the energetic impasse by leveraging intramolecular λ^3 -bromane formation with the pyrolysis reaction of the diazonium salt of 2-amino-2'-bromobiphenyl (1), obtaining cyclic o,o'-diphenylene- λ^3 -bromane (2; Figure 1A). The use of the "Martin ligand" is an excellent alternative strategy for the preparation of stable λ^3 -bromane (4; Figure 1B).^{10,11} These approaches, however, are less than ideal in terms of versatility. In 1984, Frohn and co-workers revolutionized this field by the synthesis of difluoro- λ^3 -bromane 6 (Frohn's reagent):¹² the use of the substitution reaction of BrF₃ with arylsilanes 5 circumvents the unfavorable oxidation process. Importantly, Frohn's reagent 6 serves as a pivotal platform for various λ^3 -bromanes (7; Figure 1C).^{13–18} Furthermore, difluoro- λ^3 -bromane 6 promotes unprecedented reactions owing to the hypernucleofugality of the ArBr(III)⁺ group:¹⁹ examples include Hofmann rearrange-ment of sulfonamide²⁰ and Baeyer–Villiger oxidation of primary aliphatic aldehydes.²¹ However, excessive reactivity and the need for strict exclusion of moisture (6 immediately decomposes into ArBr, HF, and O₂ via oxidation of water) have limited the utility of Frohn's protocol.¹²

We herein present the first versatile synthetic methodology for benchtop-stable λ^3 -bromanes (9 and 10) through



Figure 1. Background of $Ar-\lambda^3$ -bromane chemistry. (A) The first synthesis by Sandin and Hay. (B) Martin's bicyclic λ^3 -bromane 4. (C) Frohn's protocol. (D) This work. (E) Expected stabilization effect.

electronic and steric stabilization of the three-center fourelectron (3c-4e) hypervalent bond on the Br(III) center by using the 1,2-benzbromoxol-3-(1H)-one (BBX) ligand (Figure 1D,E).²² The similar 1,2-benziodoxol-3-(1H)-one (BIX)

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ligand has been historically used for the preparation of various λ^3 -iodanes.^{23–26} Another key to the present achievement is the use of the *N*-triflylimino group as an exocyclic changeable ligand, which can be transformed into various functionalities through electrophilic substitution reactions on the Br(III) center. This strategy allows us to synthesize a series of air/moisture/heat/light-stable λ^3 -bromanes coordinated with nitrogen, oxygen, and carbon moieties at the apical (exocyclic) position.

In order to synthesize BBX- λ^3 -bromane 9, we commenced our study by the direct oxidation of 2-bromobenzoate derivatives (8) with various oxidants (Martin's approach). However, these trials resulted in the oxidation (fluorination) of the aromatic ring or decarboxylation in preference to the desired oxidation of bromine (Scheme S1A). All attempts at ligand exchange (Frohn's approach) of arylstannanes/boranes/ silanes with BrF₃ were unsuccessful (Scheme S1B). Then, we focused on the ylide transfer reaction of imino- λ^3 -bromane 11a (Ar = *p*-CF₃C₆H₄), developed by our group in 2007,^{18,27} to *o*bromobenzoates 8. Gratifyingly, the treatment of 11a with an excess amount (50 equiv) of ethyl *o*-bromobenzoate (8a) at room temperature gave the desired *N*-triflylimino- λ^3 -bromane 12a in 79% yield (Scheme 1A). Use of trimethylsilyl *o*-

Scheme 1. Synthesis, Structure, and Reactivities of N-Triflylimino-BBX- λ^3 -bromanes (12)



bromobenzoate **8b** resulted in smooth NTf transfer accompanied by desilylation to afford the corresponding *N*triflylimino- λ^3 -bromane **12b** in 80% yield. In sharp contrast with acyclic λ^3 -bromanes, these BBX-imino- λ^3 -bromanes **12** exhibited extremely high air/moisture/thermal stability. The isolated powders **12a** and **12b** can be stored under ambient conditions of temperature, air, moisture, and lighting without decomposition for at least 4 months. Indeed, no sign of decomposition was detected in CH₂Cl₂ solution after one month.

The structures of imino- λ^3 -bromanes 12a and 12b were unambiguously determined by single-crystal X-ray diffraction analyses (Scheme 1B and Figure S2); the strong intramolecular coordination of C=O to Br (12a: 2.641(2) Å; 12b: 2.504(1) Å) is presumably responsible for the stability of the BBX- λ^3 bromanes (Figures S1 and S2). Notably, BBX- λ^3 -bromanes 12 retain strong nucleofugality of the BBX unit; a unique aziridination reaction of an olefin (13) was observed under mild conditions,^{18,28} whereas the λ^3 -iodine(III) analogue, N- pubs.acs.org/JACS

Tf-BIX- λ^3 -iodane **15** was totally unproductive (Scheme 1C). C-H amination transforms stable, abundant, and inert hydrocarbons into viable building blocks for the robust construction of C-N bonds.²⁹ BBX-imino- λ^3 -bromanes **12a** thus prepared facilitated C-H amination of cyclohexane (**16**) without any catalyst, while in marked contrast, no reaction occurred with the corresponding BIX- λ^3 -iodane **15**.

We next focused on the transformation of the imino- λ^3 -bromanes 12 to various BBX- λ^3 -bromanes (Scheme 2A).

Scheme 2. Ligand Exchange Reactions of 12



Lewis/Brønsted acid-catalyzed ligand exchange of the imino group to Tf₂C⁻ or phenyl ligand produced the corresponding bromonium ylide **18** and phenyl- λ^3 -bromane **19**, respectively, in high yields. Strong coordination of the CO₂Et ligand was revealed by ¹H/¹³C NMR spectra and X-ray crystal structure analysis (Figure S3). This may be the reason why these BBX- λ^3 -bromanes **18** and **19**, which can potentially serve as an electrophilic bis(triflyl)methylating and arylating agents, respectively, in solution,^{4,5,30-32} both turned out to be stable in the isolated form on the benchtop for at least 6 months. On the other hand, all attempts at ligand exchange to alkynyl and vinyl groups were unsuccessful; instead, preferential aziridinations of these π bonds occurred.

Gratifyingly, saponification of 12a followed by careful neutralization of the resulting sodium *o*-bromosylbenzoate (20) afforded 1-hydroxy-1,2-benzbromoxol-3(1H)-one (hydroxy-BBX- λ^3 -bromane, **21**) in 66% yield (over 2 steps; Scheme 2). Treatment of 12b with NaOH (2 equiv) also resulted in the clean formation of **20** in 97% yield. Since λ^3 bromanes with a hydroxyl ligand have never been synthesized, we will discuss in detail the physicochemical properties of 21. Evidence supporting the presence of the Br-OH bond was obtained by means of FT-IR and ¹H NMR analyses, which showed a characteristic absorption at ν 2650–2400 cm⁻¹ (solid state) and a broad signal of a proton exchangeable with D₂O at δ 7.05 ppm (in CD₃CN, 22 °C), respectively, similar to those observed with the I(III) analogue, hydroxy-BIX- λ^3 -iodane 22.³³⁻³⁵ Compound 21 showed higher solubility than 22 under the same conditions: 21 is sparingly soluble in CH₃CN, CH₃CN-H₂O, H₂O, and 1,1,1,3,3,3hexafluoro-2-propanol (HFIP), but not in less polar solvents (dichloromethane, chloroform, THF, diethyl ether, ethyl acetate, benzene, and hexanes). In solution, 21 displays a strong absorption band at $\lambda = 268-275$ nm (in CH₃CN) or at $\lambda_{\text{max}} = 278 \text{ nm}$ (in H₂O), but is transparent in the visible to NIR ($\lambda \leq 1000$ nm) region. The isolated colorless fluffy

solution (0.016 M, 22 °C), with evolution of O₂ gas. Recrystallization of 21 from 1:1 CH₃CN-H₂O at 4 °C afforded colorless prisms with a melting point of 116-117 °C (decomp.) that were suitable for X-ray crystallography (Scheme 2C and Figures S5 and S6A). Compound 21 has distinct T-shaped trigonal bipyramidal geometry around the Br(III) atom, with a near-linear O1-Br1-O3 triad $(174.43(14)^{\circ})$, and forms a five-membered ring through intramolecular Br1-O1 interaction (2.226(3) Å). All atoms (Br1, C1, C6, C7, and O1) in the five-membered ring are essentially in the same plane and the RMS atomic deviation from the least-squares plane is 0.049(5) Å. The exocyclic Br1-O3 distance of 1.824(3) Å is comparable to the predicted value for covalent radius (1.80 Å) but considerably shorter than the reported value of 2.01-2.06 Å for the Br(III)-O(Ac) bond in (diacetoxybromo)arene 7 (X = Y = OAc), owing to the trans influence on the Br(III) center.^{36–38} The presence of a hydrogen atom H1 attached to O3 could not be determined owing to low electron density, but the intermolecular O2…O3 (symmetry operation 3: -X + 1/2 + 1, Y + 1/2, Z + 1/2) distance of 2.626(5) Å strongly suggests the presence of a hydrogen atom between these two oxygen atoms with efficient hydrogen bonding. The $O-X(III)\cdots O-X(III)$ (X = Br or I) intermolecular interactions observed in the crystal structure of 22 was not seen in 21, probably due to the lower halogen-bond donor ability of Br(III) than I(III).³⁹ These structural differences are likely to be related to the solubility difference between 21 and 22 (vide supra).

refrigerator (4 °C) indefinitely, while it gradually decomposes with a half-life time $(t_{1/2})$ of 7.5 days in 1:1 CD₃CN-D₂O

Hydroxy-BBX- λ^3 -bromane 21 thus prepared turned out to serve as a potent oxidizing agent through Br(III)-OH bond activation (Scheme 3). For instance, 21 undergoes homolytic Br-OH cleavage even at room temperature. Thermolysis of 21 in benzene at 80 °C produced 2-bromobiphenyl (23; 58% yield), along with a small amount of phenol (24) (3% yield; Scheme 3A). The formation of these products strongly suggests that homolytic cleavage of the Br-OH bond and successive decarboxylation of radical I take place, resulting in the formation of 2-bromophenyl radical II. Under the same conditions, iodine(III) analogue 22 was recovered intact.⁴⁰ Further, 21 also served as an excellent radical initiator in the autoxidation of aliphatic hydrocarbons (Scheme 3B). Exposure of indane to 21 in CH₂Cl₂ at 40 °C under oxygen afforded 1indanone (25) in moderate yield; the initial hydrogen abstraction from indane is mediated by the Br radical I, and hence, 2-bromobenzoic acid (26) is exclusively produced. Encouraged by this, we next investigated autoxidation of cyclohexane, which has a much higher bond dissociation energy (benzylic C-H in indane: 85.9 kcal/mol vs Cy-H: 99.5 kcal/mol).⁴¹ This process is extremely important in industry (as the first step of 6-nylon/6,6-nylon synthesis) and generally requires a transition metal catalyst such as Co(III) at elevated temperature and/or high pressure of O2.42 Pleasingly, 21 could effectively initiate autoxidation of cyclohexane at 80 °C in air (1 atm), and after 24 h, a 57:43 mixture of cyclohexanol (27) and cyclohexanone (28)(so-called KA oil) was obtained in 82% yield along with cyclohexyl hydroperoxide (29; 67%). In addition, 21 functions as a nonradical oxygen transfer agent (Scheme 3C). For instance, 21 oxidizes diphenyl

Scheme 3. Reactions of 21 with Various Nucleophiles*

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^{*}Yields were determined by ¹H NMR. ^{*a*}Isolated yields. ^{*b*}Yields of autoxidation products **27–29** are calculated based on **21**. ^{*c*}The ¹⁹F NMR yield.

sulfide at room temperature under argon to give the corresponding sulfoxide **30** in 92% yield. The absence of overoxidized diphenyl sulfone as well as the dependence of the rate on the concentration of sulfide suggest that **21** serves as an electrophilic oxygen donor.⁴³ In the presence of base, oxidation of $\alpha_{,\beta}$ -unsaturated ketone to afford epoxide **31** proceeded at room temperature in high yield. This reaction probably involves Michael addition of **21**, followed by reductive elimination, as an electron-withdrawing group accelerated the rate of oxidation.^{44,45} Oxidation of weakly nucleophilic HFIP with **21** proceeded at room temperature via a ligand exchange-reductive elimination sequence, based on the ¹H NMR/ESI-MS data (Figure S8). None of these transformations proceeded to a discernible extent with iodine(III) analogue **22** under the same reaction conditions.

Next, the potential to further transform the hydroxy-BBX- λ^3 bromane (21) into various λ^3 -bromanes was examined (Scheme 4). Quantitative acetylation of 21 with acetic anhydride proceeded at room temperature to give acetoxy-BBX- λ^3 -bromane 33. More interestingly, treatment of 21 with in situ-generated alkynyl(difluoro)borane 34 followed by alkaline hydrolysis selectively afforded β -(triisopropylsilyl)ethynyl-BBX- λ^3 -bromane 35 in 30% yield. In marked contrast to acyclic analogues,^{13,38} BBX- λ^3 -bromanes 33 and 35 can be handled under ambient conditions without decomposition.⁴⁶

In conclusion, our use of the BBX group opens up a new strategy for the synthesis of λ^3 -bromanes that overcomes the requirement for strict exclusion of moisture under dark and

Scheme 4. Synthesis of Acetoxy- (33) and Alkynyl- λ^3 bromane (35)



cryogenic conditions normally demanded by the use of λ^3 bromanes. The BBX strategy has enabled the isolation of various λ^3 -bromanes with heteroatom/carbon ligands, which is a long-cherished dream in the field of hypervalent bromine-(III) chemistry. Some synthetic applications of this approach have been demonstrated. We believe our BBX strategy represents a fundamental advance in the preparation of λ^3 bromanes, and will have broad synthetic utility. Indeed, its practical convenience and efficiency should make it widely applicable both in the laboratory and in industry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c04536.

Experimental procedures and characterization data (PDF)

Accession Codes

CCDC 2072450, 2076045, 959764, 959765, and 959767– 959769 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_ request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

- Kazunori Miyamoto Graduate School of Pharmaceutical Sciences, The University of Tokyo, Tokyo 113-0033, Japan; Graduate School of Pharmaceutical Sciences, University of Tokushima, Tokushima 770-8505, Japan; orcid.org/ 0000-0003-1423-6287; Email: kmiya@mol.f.u-tokyo.ac.jp
- Masanobu Uchiyama Graduate School of Pharmaceutical Sciences, The University of Tokyo, Tokyo 113-0033, Japan; Research Initiative for Supra-Materials (RISM), Shinshu University, Ueda 386-8567, Japan; orcid.org/0000-0001-6385-5944; Email: uchiyama@mol.f.u-tokyo.ac.jp

Masahito Ochiai – Graduate School of Pharmaceutical Sciences, University of Tokushima, Tokushima 770-8505, Japan; Email: bmasahito@gmail.com

Authors

Motomichi Saito – Graduate School of Pharmaceutical Sciences, University of Tokushima, Tokushima 770-8505, Japan

Shunsuke Tsuji – Graduate School of Pharmaceutical Sciences, University of Tokushima, Tokushima 770-8505, Japan pubs.acs.org/JACS

Taisei Takagi – Graduate School of Pharmaceutical Sciences, The University of Tokyo, Tokyo 113-0033, Japan Motoo Shiro – Rigaku Corporation, Akishima, Tokyo 196-

8666, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.1c04536

Author Contributions

^{II}These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

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(45) Results of a preliminary study on the rate of epoxidation, see Table S1 in the Supporting Information.

(46) In solution, **35** gradually decomposed, probably via protodesilylation (see Supporting Information).

NOTE ADDED AFTER ASAP PUBLICATION

This paper originally published ASAP on June 14, 2021. An update to the Supporting Information was made regarding the large-scale synthesis of **12b** and a new version was posted on June 16, 2021.