
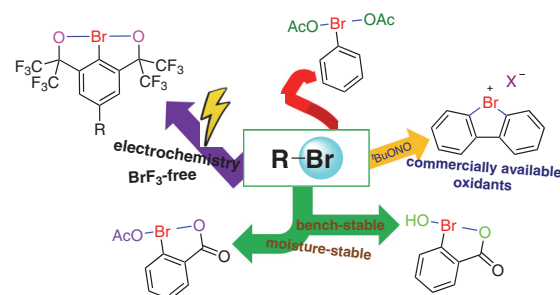


Hypervalent Bromine(III) Compounds: Synthesis, Applications, Prospects

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Abstract Hypervalent compounds play a prominent role in homogeneous oxidation catalysis. Despite the higher reactivity of hypervalent bromine compounds when compared to their isoelectronic iodine analogues, the corresponding λ^3 -bromanes are much less explored. This can be attributed to the discernible lack of convenient strategies for their synthesis. This short review highlights the available methods for the synthesis of various organo- λ^3 -bromanes, with a major focus on the recent developments and reactivities in the last few years. Additionally, limitations and future prospects of hypervalent bromine chemistry are discussed.

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Key words λ^3 -bromanes, hypervalent, bromine, iodine, bromonium, Br(III), Oxidation

1 Introduction

In marked contrast to the substantial growth in the field of iodine(III) reagents, their isoelectronic hypervalent bromine counterparts have seen notably slower progress. During the last century, only a reserved selection of scientists have partaken in their development, resulting in their limited precedence in the literature. While the first ever synthesis of a hypervalent iodine compound, (dichloro-



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iodo)benzene, was reported in 1886 by Willgerodt,¹ the first hypervalent bromonium compound arrived notably later, in 1952, when Sandin and Hay reported the preparation of a bromonium salt through the intramolecular nucleophilic bromine attack on an aryldiazonium salt.² Still, the remarkably slower growth of hypervalent bromine chemistry cannot be justified by its later arrival 'on the market'. In line with this, we will highlight both the predominant struggles in terms of the synthetic approaches that have heavily hindered progression in this field, as well as the attractive properties of bromine(III) compounds, in an effort to incentivize scientific interest.³

Hypervalency refers to a main group element, such as hypervalent bromine, that breaks the octet rule and has more than 8 electrons in its valence shell.⁴ According to IUPAC rules, compounds with non-standard bonding numbers are given a λ notation. For example, H_3Br is called λ^3 -bromane and has a dectet structure, while H_5Br is called λ^5 -bromane with a dodecet structure.

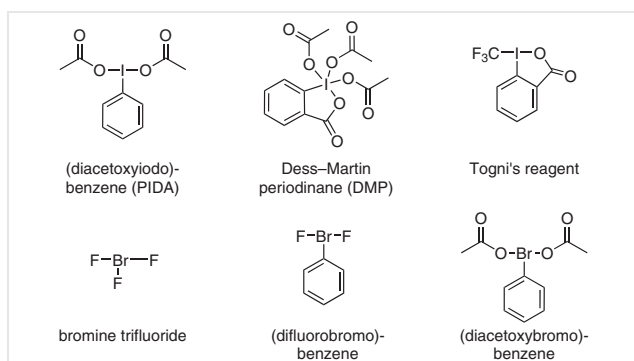


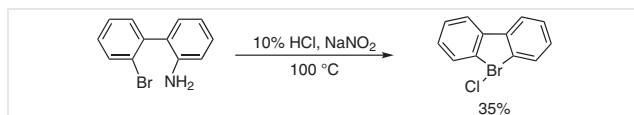
Figure 1 Commonplace hypervalent iodine/bromine compounds

Hypervalent-halogen-containing compounds have attracted unprecedented attention in organic chemistry, which has been attributed to their unique characteristic properties.⁵ Undoubtedly, the vast majority of this attention has been paid to the field of iodine chemistry, with reagents such as Dess–Martin periodinane,⁶ [bis(trifluoroacetoxy)iodo]benzene, (diacetoxyiodo)benzene and diaryliodonium-type compounds⁷ becoming mainstream reagents in contemporary organic synthesis and even commercially available (Figure 1). The attractiveness of iodine(III) reagents can be accredited to their versatile characteristics; they are a mild, non-toxic (green oxidation), easy to handle and environmentally benign class of reagents. The reactivity pattern of hypervalent iodine is somewhat discretely similar to the heavy transition metals and, as such, they are typically preferred as a less toxic alternative. The diverse nature of these reactions includes oxidative couplings,⁸ halogenations,⁹ arylations,¹⁰ oxidative rearrangements,¹¹ trifluoromethylations¹² and C–H functionalizations.¹³ Their hypervalent bromine analogues can feature superior reactivity owing to their higher nucleofugality, ionization potential and stronger electrophilicity.¹⁴ Unsurprisingly, these superior qualities have facilitated the development of other useful synthetic transformations including the Bayer–Villiger-like oxidations of open-chain aliphatic aldehydes,¹⁴ metal-free C–O and C–N couplings,¹⁵ the oxidative coupling of alkynes and 1° alcohols,¹⁶ metal-free aminations of unactivated alkanes¹⁷ and thermal solvolysis,¹⁸ amongst others. Even so, despite their often superior reactivity and unique structures, a limited number of hypervalent bromine reagents have been reported and utilized, especially in comparison to hypervalent iodine reagents.

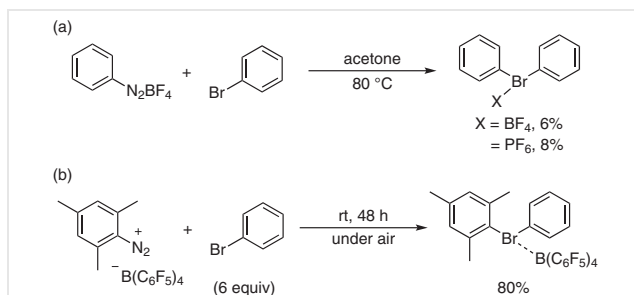
Perhaps the most substantial impediment to progression in this field can be attributed to the discernible lack of expedient methods for the synthesis of these compounds. The main challenge arises due to the innate thermodynamic barrier for the oxidation of bromine(I) to hypervalent bromine. For instance, the oxidation potentials of aryl bromides [o -(CO_2Et) $\text{C}_6\text{H}_4\text{Br}$ = 2.3 V vs Ag/0.01 M AgCl in MeCN] are remarkably high in comparison to iodides [o -(CO_2Et) $\text{C}_6\text{H}_4\text{I}$ = 1.9 V vs Ag/0.01 M AgCl in MeCN], arising from their greater electronegativity and ionization potential.¹⁹ Hereby, the oxidation of the corresponding haloarenes with oxidants, which is standard for the preparation of iodine(III) reagents, is generally not effective for the synthesis of hypervalent bromanes. Until recently, the most competent synthesis of hypervalent bromine compounds involved the ligand exchange of bromine trifluoride (BrF_3), which circumvents the unfavorable oxidation process. These approaches, however, are far from ideal in terms of safety and convenience. Bromine trifluoride is a highly reactive compound that etches glass and quartz, sets fire to paper and wood, and reacts violently with the majority of organic compounds.²⁰ Literature protocols for its access can be low yielding and require harsh reaction conditions. The choice of solvent is also pivotal in terms of solubility and stability, but is often not typical in terms of organic chemistry. For instance, BF_3 reacts violently with CH_2Cl_2 at temperatures above -20°C .²¹ It is moderately soluble in trichlorofluoromethane, but above 5 – 10°C it reacts with CCl_3F to produce CCl_2F_2 , mainly. Moreover, the strict exclusion of air and moisture, immoderate reactivity and extreme toxicity of this reagent means specialist knowledge is required for such reactions. The poor stability of the subsequently prepared bromine(III) reagents regularly complicates matters further. For example, Frohn's reagent, a key building block for various λ^3 -bromanes, decomposes immediately in the presence of moisture via H_2O oxidation.²² Evidently, the development of user-friendly synthetic approaches, in terms of experimental safety, ease and proficiency, could provide significant incentive for the influx of new researchers into this field, which is key to rapid progression. High yielding and milder reaction conditions to access bromine(III), with a particular focus on precluding the need for fluorinating reagents, has been the focus of research in the past 5 years. Pleasingly, electrochemical oxidation, single-step oxidation with commercially available organic oxidants, and bench-stable reagents have all emerged recently. Herein, we will discuss the synthetic approaches towards bromine(III) reagents, with an emphasis on the advances in synthetic strategies that have arisen in the past 5 years. In this respect, we will highlight synthetic methods from the early 19th century and modern progressive techniques, to allow comparison between modern-day literature and the early endeavors.

2 Diaryl- λ^3 -bromanes

In pioneering work by Sandin and Hay, the first synthesis of an organo- λ^3 -bromane was reported through the thermal decomposition of the aryldiazonium salt, readily prepared from 2-amino-2'-bromobiphenyl (Scheme 1).² Interestingly, the first organo- λ^3 -chlorane was also synthesized using a similar strategy. In this work, the close proximity of the adjacent halogen atom was crucial to capture the generated aryl cation in an intramolecular fashion. In this respect, adoption of an almost identical strategy for the intermolecular diaryl- λ^3 -bromane synthesis was largely unsuccessful, only resulting in low yields of the desired products (Scheme 2).^{23,24} Encouragingly, the efficiency of trapping the aryl cation has recently been improved significantly by employing a weakly coordinating ligand/counter anion along with the mesityl diazonium salt.²⁵

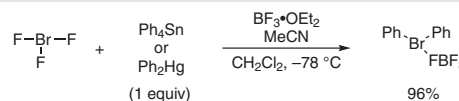


Scheme 1 Synthesis of the first hypervalent organo- λ^3 -bromane



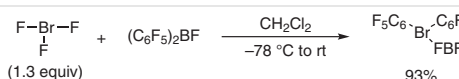
Scheme 2 Initial and modified attempts for the synthesis of acyclic diaryl- λ^3 -bromanes

Later, in 1980, in a significant breakthrough, Nesmeyanov and co-workers developed a more general pathway for the synthesis of acyclic diaryl- λ^3 -bromanes. In this approach, the highly reactive bromine trifluoride (BrF_3) underwent double ligand exchange on the bromine(III) center with aryl groups, deriving from tetraarylstannane or diarylmercury compounds in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ (Scheme 3).²⁶ Such ligand exchange with a nucleophile is believed to follow an addition–elimination sequence similar to iodine(III) analogues. The role of acetonitrile in this reaction is proposed to solubilize and stabilize the highly reactive BrF_3 and decrease the oxidizing ability of the bromine(III) through $\text{BrF}_3 \cdot (\text{MeCN})_2$ complex formation. The Lewis acid $\text{BF}_3 \cdot \text{OEt}_2$ was used to facilitate the second F/Ar exchange. Later, this approach was successfully extended for the use of aryl silanes,²⁷ and even arenes,²⁸ in place of tetraarylstannanes in acyclic diaryl- λ^3 -bromane synthesis.



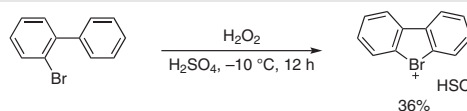
Scheme 3 Intermolecular diaryl- λ^3 -bromane synthesis

The use of $\text{BF}_3 \cdot \text{OEt}_2$ as an exogenous Lewis acid could be avoided when the Lewis acidic aryl-transfer reagent $(\text{C}_6\text{F}_5)_2\text{BF}$ was used. However, this strategy is limited by the generality in aryl-transfer reagent (Scheme 4).²⁹ From the crystal structure, an infinite $-\text{Br}-\text{F}-\text{B}-\text{F}-$ zigzag chain structure was observed for bis(perfluorophenyl)bromane tetrafluoroborate and the bromine(III) center exhibited a distorted square-planar coordination.



Scheme 4 External Lewis acid free intermolecular diaryl- λ^3 -bromane synthesis

Acyclic diaryl- λ^3 -iodanes can be synthesized by simple oxidation of an iodoarene by an oxidant in the presence of another arene. However, such an approach is not suitable for isoelectronic diaryl- λ^3 -bromanes owing to the lower polarizability of the bromine atom.³⁰ However, a few reports can be found where 2-bromobiphenyl derivatives afford the desired λ^3 -bromane through oxidation by either hydrogen peroxide in H_2SO_4 (Scheme 5)³¹ or by $\text{H}_2\text{S}_2\text{O}_8$ generated in situ from a $\text{K}_2\text{S}_2\text{O}_8/\text{H}_2\text{SO}_4$ combination.³²

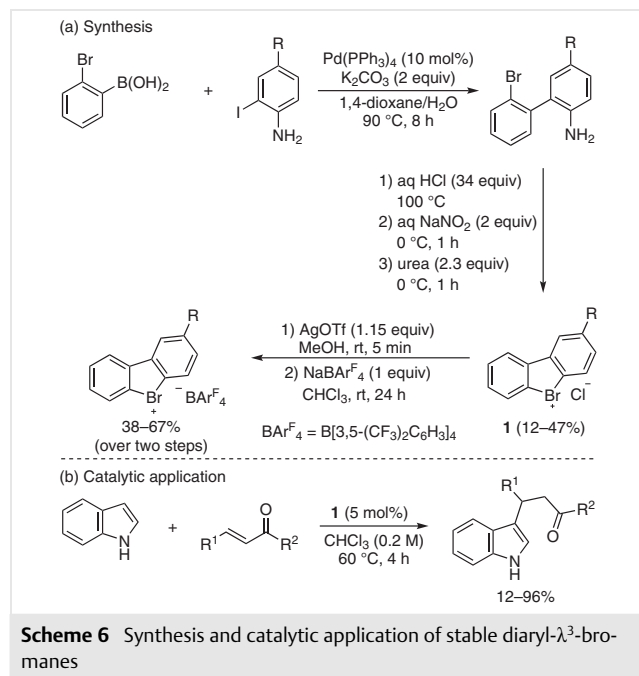


Scheme 5 Arene-oxidation-induced diaryl- λ^3 -bromane synthesis

Despite all these efforts, the synthesis of diaryl- λ^3 -bromanes is still challenging since BF_3 is necessary in most cases. BrF_3 -free methods are low yielding and are typically limited to intramolecular versions only.

Recently, in a seminal report by Yoshida and co-workers, a modified procedure for the BrF_3 -free synthesis of cyclic diaryl- λ^3 -bromanes was disclosed. In this case, a series of functionalized 2-amino-2'-bromobiphenyl derivatives was easily synthesized through palladium-catalyzed Suzuki coupling reactions. Next, these biphenyl derivatives were successfully cyclized via their corresponding diazonium salts to produce the diarylbromonium salts (Scheme 6). From the crystallographic analysis of the chloride salt, the existence of an ion pair was unambiguously established in place of the covalent bond as initially predicted in Scheme 1. The ionic nature was further confirmed by successful counter anion exchange with triflate and the bulky BAr^{F}_4 [$\text{Ar}^{\text{F}} = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3$]. In perhaps the most impressive feat,

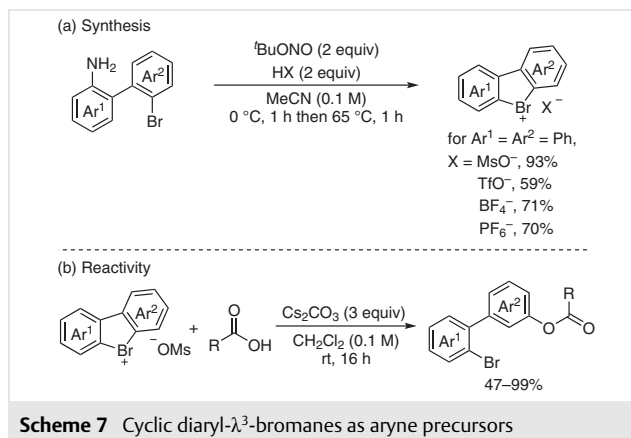
Yoshida utilized these stable bromonium salts as halogen-bonding organocatalysts in the Michael addition of indoles to α,β -unsaturated ketones.^{18b} So far, this is the first and only catalytic application of a λ^3 -bromane in synthesis.



Scheme 6 Synthesis and catalytic application of stable diaryl- λ^3 -bromanes

Furthermore, in an important breakthrough in recent years, Wencel-Delord and co-workers developed a general and safe strategy for the synthesis of cyclic diaryl- λ^3 -bromanes with significantly improved yields. The use of *tert*-butyl nitrite ($t\text{BuONO}$) as a mild oxidant in the presence of a Brønsted acid was key to generate these bromonium salts in high yields (Scheme 7).¹⁵ Subsequently, these bromonium salts were found to form arynes in the presence of a weak base. Such arynes could be trapped by a carboxylic acid or amine to deliver the formal *meta*-selective transition-metal-free C–O and C–N coupling products. Typically, λ^3 -iodanes can display such reactivity only in the presence of a transition metal, emphasizing the superior qualities of hypervalent bromine reagents.³³ However, a recent report disclosed that λ^3 -iodanes can show similar reactivity in the presence of strong bases.³⁴

Apart from such newly discovered unique reactivity profiles, in general, diaryl- λ^3 -bromanes serve as more efficient arylating reagents than their λ^3 -iodane analogues. They present as excellent arylating reagents towards various heteroatom nucleophiles (O, N, S, halide, etc.) under mild reaction conditions. In general, the reactivity towards harder nucleophiles follows the order: $\text{Ph}_2\text{I}^+ < \text{Ph}_2\text{Br}^+ < \text{Ph}_2\text{Cl}^+$ owing to the enhanced nucleofugality along the sequence.³⁵ In general, for 4-substituted unsymmetrical diaryl- λ^3 -bromanes, nucleophiles prefer to attack a phenyl ring carrying electron-withdrawing groups. However, for 2-substituted



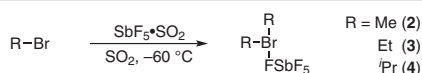
Scheme 7 Cyclic diaryl- λ^3 -bromanes as aryne precursors

unsymmetrical diaryl- λ^3 -bromanes, an *ortho* effect plays a crucial role and the 2-substituted phenyl ring is attacked by the incoming nucleophile.^{24,36}

3 Dialkyl- λ^3 -bromanes

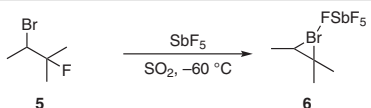
Dialkyl- λ^3 -bromanes are powerful alkylating reagents in organic chemistry. However, given the lack of reports in recent years, this short section proves to merely introduce the reader to their existence, benefits and synthetic problems. Alkyl- λ^3 -bromanes are generally considered as unstable transient intermediates. As a result, only a limited number of methods are known for their synthesis and characterization. Open-chain dialkyl and alkyl(aryl)- λ^3 -bromanes were largely unknown until the late 20th century. In 1969, the first symmetrical dialkyl and alkyl(aryl)- λ^3 -bromanes were reported by Olah and DeMember through the self-condensation of alkyl halides with a strong Lewis acid, such as SbF_5SO_2 , under inert atmospheres at low temperatures (Scheme 8).³⁷ The formation of dimethyl, diethyl and diisopropyl(hexafluoroantimonato)- λ^3 -bromanes was confirmed by low-temperature NMR, IR, and laser Raman spectroscopy.³⁸ Symmetrical dialkylhalonium ions could be obtained by the reaction of alkyl halides with an excess of SbF_5SO_2 , anhydrous fluoroantimonic acid ($\text{HF}\cdot\text{SbF}_5$) or anhydrous silver hexafluoroantimonate in SO_2 solution. Both symmetrical and unsymmetrical dialkylhalonium ions could be obtained by the alkylation of alkyl halides with methyl or ethyl fluoroantimonate in SO_2 solution. Dialkylhalonium salts prepared this way were generally clean and not contaminated with any by-products. While the reactions of alkyl fluoroantimonates with methyl-, ethyl- or diisopropyl bromide gave the corresponding dialkylhalonium ions, the reactions of tertiary alkyl halides gave an alkylcarbenium ion and a symmetrical dialkylhalonium ion. Both unsymmetrical and symmetrical dialkylhalonium compounds undergo immediate hydrolysis in atmospheric moisture, which hampers their practicality. Moreover, the

non-symmetrical λ^3 -bromanes were kinetically labile and susceptible to disproportionation and self-condensation, even at low temperature ($-30\text{ }^\circ\text{C}$). In general, the relative stability of the prepared dialkylhalonium ions follows the order $\text{RI}^+\text{R} > \text{RBr}^+\text{R} > \text{RCI}^+\text{R}$, indicating that the larger halogen atom was more capable of accommodating the charge. Despite the instability, compound **2** could be isolated as a storable solid at room temperature under argon. The chemical reactivity as well as synthetic application of the prepared dialkylhalonium ions was demonstrated by the alkylation of π -donor aromatics, olefins and a wide variety of n -donor bases. For example, compounds **2** and **3** facilitated the Friedel–Crafts alkylation of benzene or toluene at $-50\text{ }^\circ\text{C}$ in SO_2ClF within 5 minutes, and the isomer distributions showed no significant differences from typical Friedel–Crafts reactions. Notably, dimethyl- λ^3 -iodane could not facilitate the same reaction, even at $20\text{ }^\circ\text{C}$, emphasizing the increased reactivity of the dialkyl- λ^3 -bromanes compared to the corresponding iodanes. Nevertheless, further investigation of these types of compounds is mainly restricted by their facile decomposition.



Scheme 8 Synthesis of dialkyl- λ^3 -bromanes

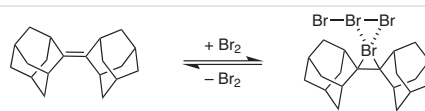
In 1937, Roberts and Kimball first proposed that a cyclic three-membered bromonium ion was formed as an intermediate during the electrophilic addition of Br_2 to a double bond.³⁹ Subsequently, similar reactions have been invoked for the preparation of cyclic dialkyl- λ^3 -bromanes. Olah and Bollinger presented the synthesis of a cyclic dialkyl- λ^3 -bromane **6** by treating 2-fluoro-3-bromo-2-methylbutane (**5**) with SbF_5 in a sulfur dioxide solution at $-60\text{ }^\circ\text{C}$ (Scheme 9).⁴⁰



Scheme 9 Synthesis of a cyclic dialkyl- λ^3 -bromane by Olah and co-workers

When 2-fluoro-3-bromo-2-methylbutane was ionized in a SbF_5SO_2 solution at $-78\text{ }^\circ\text{C}$, a stable solution of the (trimethyl)ethylenebromonium ion was obtained. Although NMR evidence for the existence of such species was reported, solid-state structures for the λ^3 -bromane were not since subsequent nucleophilic attack to yield the product was rapid. In terms of modern synthetic developments, these procedures have diminished appeal, particularly in terms of safety. Antimony pentafluoride and its derivatives are high-

ly corrosive chemicals that require specialist equipment for handling, which limits the user-friendliness of such techniques. Later, Brown and co-workers reported the solid-state structure of a three-membered cyclic λ^3 -bromane, notably in the absence of SbF_5 (Scheme 10).⁴¹ The bromination of adamantylidene adamantane in chlorinated hydrocarbons yielded a bright yellow solid, which could be easily handled without special precautions. This compound was unstable in polar protic solvents and tended to lose Br_2 , converting back into the starting alkene, but it had both stability and modest solubility in MeCN, MeNO₂, and dichloroethane. In this case, the incorporation of the adamantyl group was to sterically shut down subsequent nucleophilic substitution reactions.

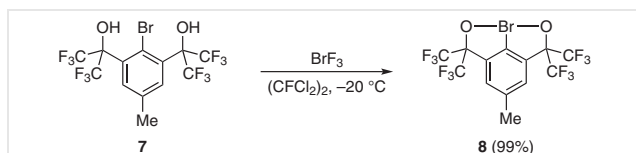


Scheme 10 Structure of a three-membered cyclic λ^3 -bromane synthesized by Brown and co-workers

Overall, in recent years, there has been no significant progression in the synthesis of dialkyl- λ^3 -bromanes, despite their synthetic prowess. Given their emergence as powerful alkylating reagents, certainly a safer, more stable, and versatile bromine(III)-type alternative to these reagents would be of huge progress to this area.

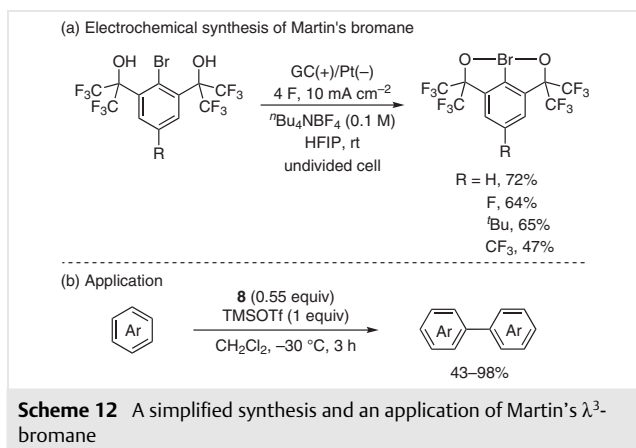
4 Dihetero- λ^3 -bromanes

As outlined in the previous two sections, the stability of organo- λ^3 -bromanes is dependent on the presence of aryl groups with a bromine(III) center. To complement this, several attempts were made to investigate the synthesis and reactivity of dihetero- λ^3 -bromanes containing one aryl group. The first report on dihetero- λ^3 -bromane synthesis came from the Martin group in 1980. In this case, highly reactive liquid BrF_3 was employed to oxidize the bromoarene **7** in $(\text{CFCl}_2)_2$ at a low temperature for the generation of air- and moisture-stable solid **8** (Scheme 11).⁴² The crystal structure revealed two inequivalent O–Br bonds with lengths slightly longer than the equivalent covalent bond lengths (1.81 Å). The two appended 'Martin' alkoxy ligands bind in the apical site of the bromine(III) center to form linear O–Br–O hypervalent bonding. An intermolecular oxygen binding to the Lewis acidic bromine(III) center from another molecule forms an overall dimeric structure and provides higher stability.⁴³ Compound **8** can tolerate mild acidic or basic conditions. Also, it can oxidize heteroatomic nucleophiles such as PhSH , PhNH_2 , NaI , HBr , etc.



Scheme 11 Synthesis of a stable dialkoxyaryl- λ^3 -bromane

Despite its high stability, an important limitation of Martin's λ^3 -bromane is the use of BrF_3 . In 2021, this issue was addressed by Francke, Suna and co-workers. In this ground-breaking example, the simple electrochemical oxidation of aryl bromides possessing two coordinating hexafluoro-2-hydroxypropanyl substituents delivered stable λ^3 -bromane derivatives in high yields (Scheme 12).⁴⁴

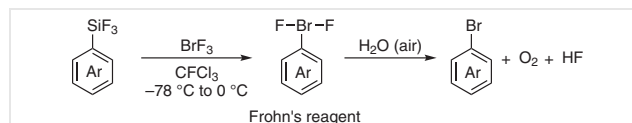


Scheme 12 A simplified synthesis and an application of Martin's λ^3 -bromane

With just the use of an undivided cell under constant current conditions, and with glassy carbon (GC) as the working electrode, platinum as the counter electrode, TBABF_4 as the supporting electrolyte and HFIP (hexafluoroisopropanol) as the solvent, the easy scale up for the synthesis of a bench-stable λ^3 -bromane on multi-gram scale was possible. Moreover, the reactivity of such λ^3 -bromanes was investigated for oxidative C–C, C–N, and C–O bond forming reactions to complement this simplified synthetic route. The reactivity of Martin's λ^3 -bromane is sufficient for oxidative amidation and benzoxazole formation and could be further enhanced by Lewis or Brønsted acid additives, as demonstrated by its successful application in biaryl coupling.

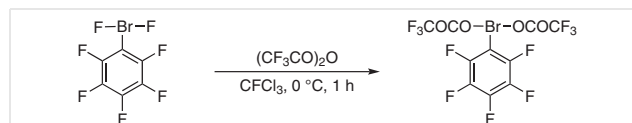
Excluding Martin's λ^3 -bromane, the chemistry of difluoro- λ^3 -bromanes is quite well established in the literature. In 1984, Frohn and co-workers revolutionized the field of hypervalent bromine chemistry by introducing difluoro- λ^3 -bromanes. These were prepared from aryl silanes and BrF_3 through ligand exchange (Scheme 13).^{22,27} In the absence of any other convenient procedure, Frohn's reagent serves as a pivotal platform for the synthesis of various λ^3 -bromanes without using highly reactive BrF_3 in subsequent steps. Generally, Frohn's reagents are stable at room temperature,

but require an inert atmosphere to prevent instantaneous decomposition into O_2 , HF and the corresponding bromoarenes in the presence of atmospheric moisture. The fluorine ligands can be easily displaced by any other nucleophiles which are stable against oxidation. Easily oxidized substrates such as aromatic alcohols and aldehydes are often converted into fluoromethyl aryl ethers⁴⁵ and difluoromethyl aryl ethers,⁴⁶ respectively, after oxidation followed by 1,2-aryl migration.



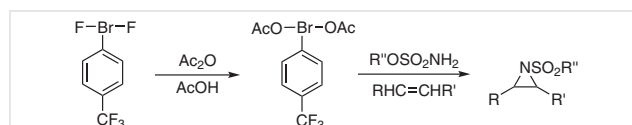
Scheme 13 Synthetic route towards difluoro- λ^3 -bromanes and their decomposition pathway

In a sharp contrast to the high stability and applicability of diacyloxy- λ^3 -iodanes, the use of diacyloxy- λ^3 -bromanes is mainly limited by their high moisture sensitivity. [Bis(trifluoroacetoxy)]- λ^3 -bromane was first synthesized by Frohn and Giesen from Frohn's reagent through ligand exchange with trifluoroacetic anhydride (Scheme 14).²² However, its reactivity was not explored.



Scheme 14 Synthesis of bis(trifluoroacetoxy)bromoarene

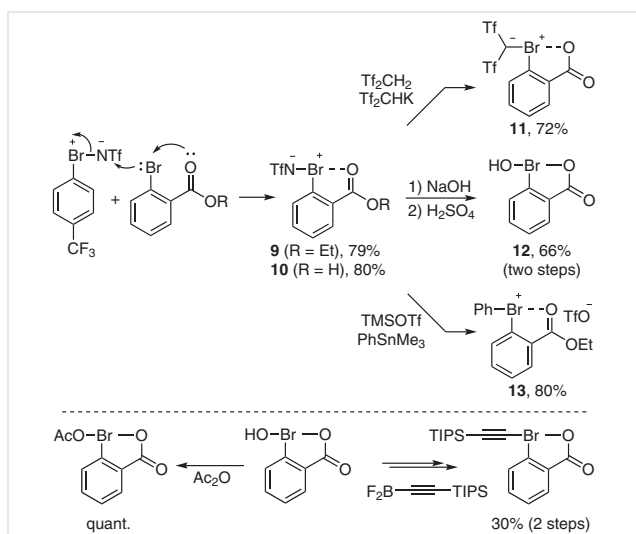
Later, Ochiai and co-workers followed a similar procedure to synthesize the corresponding acetoxy derivative. Such compounds are discretely similar to the very stable, heavily utilized and commercially available (diacetoxy-iodo)benzenes. They explored the reactivity of this diacetoxybromoarene in alkene aziridination reactions (Scheme 15).⁴⁷ The aziridination reaction proceeds with TfNH_2 or sulfamate esters in a highly stereospecific fashion with retention of the stereochemistry in olefins at room temperature by using the olefins as the limiting reagents. Interestingly, (diacetoxybromo)arenes were also used in C–H amination reactions of alkanes in the presence of a suitable sulfonamide source.⁴⁸



Scheme 15 Synthesis and reactivity of a (diacetoxybromo)arene

In a seminal report in 2021, Miyamoto, Ochiai and co-workers reported the synthesis of air/moisture-stable λ^3 -bromanes (Scheme 16).¹⁹ The methodology represents the first versatile synthetic procedure towards the synthesis of

bench-stable λ^3 -bromanes. Analogous to Martin's approach, the bromine(III) center is effectively stabilized by intramolecular R–Br–O bonding, both electronically and sterically, but in this case via a 1,2-benzbromoxol-3-(1*H*)-one (BBX) ligand. The clever use of a *N*-triflylimino group as an exocyclic changeable ligand allowed the introduction of diverse functionalities through electrophilic substitution reactions on the bromine(III) center. Using this strategy, a variety of Br-hydroxy, -acetoxy, -alkynyl, -aryl, and bis[(trifluoromethyl)sulfonyl]methylidene λ^3 -bromane derivatives were prepared. Intriguingly, all of these λ^3 -bromanes were found to be air-, moisture-, and bench-stable. The extra stabilization of the bromine(III) center by intramolecular R–Br–O hypervalent bonding was further confirmed by X-ray crystallography and NMR and IR spectroscopy of *N*-triflylimino- λ^3 -bromane. The hydroxy-BBX- λ^3 -bromane could be stored in a refrigerator (4 °C) indefinitely, though it slowly decomposes with a half-life ($t_{1/2}$) of 7.5 days in CD₃CN/D₂O (1:1) solution with evolution of O₂ gas.



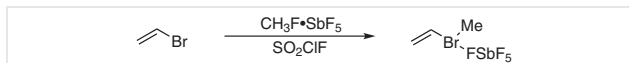
Scheme 16 Synthesis of air- and moisture-stable λ^3 -bromanes

The initial reactivity of these compounds was also investigated for the oxidation of various nucleophiles. The hydroxy-BBX- λ^3 -bromane served as a potent oxidizing reagent through the homolysis of the bromine(III)–OH bond.

5 Alkenyl- λ^3 -bromanes

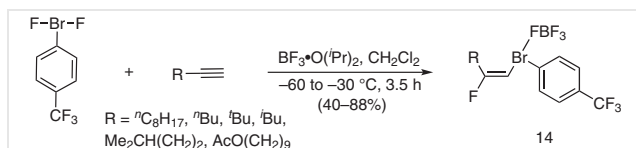
Hypervalent 1-alkenyl(phenyl)- λ^3 -iodanes demonstrate rich chemistry in modern organic synthesis.⁴⁹ The tenacious leaving group affinity of phenyl- λ^3 -iodanyl groups mean they serve as superb precursors for the generation of alkylidene carbenes and undergo unusual vinylic nucleophilic

displacement by a wide array of nucleophiles.⁵⁰ On the other hand, the chemistry of the analogous alkenyl- λ^3 -bromanes has been remarkably under explored in comparison because user-friendly synthetic methods are not well-established. Most of the proficient synthetic techniques towards these compounds rely on difluoro- λ^3 -bromanes as key reagents, yielding alkenyl- λ^3 -bromanes, often with limited stability. Their thermal stability varies over a broad range depending on the nature of the ligands and propensity for polymerization. From an historical perspective, the first preparation of an alkenyl- λ^3 -bromane was performed in 1985 by Olah and co-workers, which was only characterized by NMR.⁵¹ The method proceeded via the alkylation of the corresponding vinyl bromides (Scheme 17). For instance, treatment of vinyl bromide, in SO₂ClF at –78 °C, with a fourfold excess of freshly prepared CH₃F·SbF₅ complex, yielded a yellow-colored solution of methyl(vinyl)- λ^3 -bromane, the ¹³C NMR spectrum of which at –90 °C showed three absorptions at 132.9 (C_β), 120.9 (C_α) and 44.1 (Me) ppm. Similarly, the ethylvinyl bromonium ion was prepared by using the CH₃CH₂F·SbF₅ complex in a SO₂ solution. However, these alkenyl- λ^3 -bromanes were unstable due to their high tendency for polymerization and they consequently decomposed over several hours (roughly 4 h), even at –78 °C. Facile anti-β-elimination of the hydrogen and bromanyl group, yielding the corresponding alkynes, is the rationality behind the low thermal stability of such reagents. Hence, because of the lack of stability of such compounds, they were not demonstrated in synthetic applications.



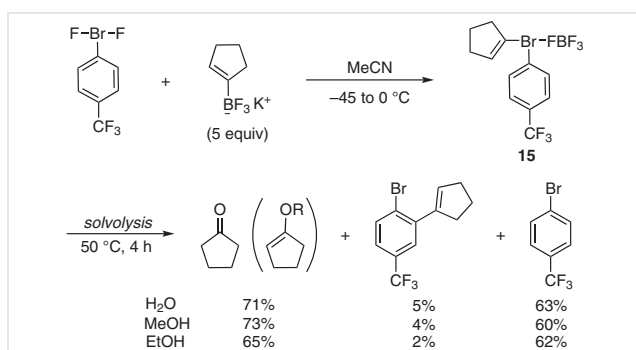
Scheme 17 The first preparation of an alkenyl- λ^3 -bromane

Noteworthy, the corresponding alkenyl- λ^3 -iodanes could not be prepared under these conditions due to the preferential oxidation of vinyl iodides. In reality, this method has relatively low practical value for application because of the low stability and tedious preparation of such compounds. But, considering the sustained success in the development of procedures for the synthesis of alkenyl- λ^3 -bromanes, it is obvious that the work served as a pivotal building block for the development of these compounds. Procedures following the ligand exchange of difluoro- λ^3 -bromanes with alkynes generally afford the alkenyl- λ^3 -bromanes in greater yields compared to the alkylation of vinyl bromides. The first fully characterized, stable alkenyl- λ^3 -bromanes were prepared by Ochiai, Frohn and colleagues in 2005 from difluoro- λ^3 -bromanes and the corresponding alkynes (Scheme 18).⁵² In marked contrast to the Olah's efforts, the prepared (*E*)-β-halovinyl(aryl)- λ^3 -bromanes **14** had much higher thermal stabilities and could even be stored at ambient temperature.



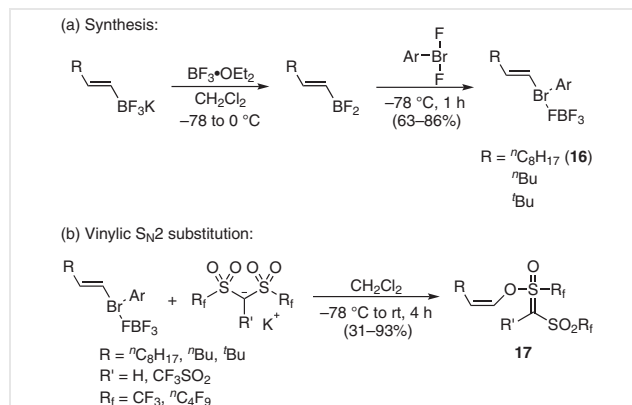
Scheme 18 The first fully characterized, stable alkenyl- λ^3 -bromanes prepared by Frohn and colleagues in 2005

In this reaction, exposure of 1-decyne to difluoro- λ^3 -bromane (1.5 equiv) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.5 equiv) at -78 °C in dichloromethane under argon yielded 62% of β -fluoro-1-deceny- λ^3 -bromane stereoselectively in an *E/Z* ratio of 96:4, after repeated decantation with hexane. (*E*)- β -Ethoxy (7%) and (*E*)- β -chloro-1-deceny- λ^3 -bromane (4%) were obtained as by-products. The β -ethoxy group originated from $\text{BF}_3 \cdot \text{OEt}_2$, so the formation of β -alkoxybromanes could be limited using the more sterically demanding $\text{BF}_3 \cdot \text{O}(\text{iPr})_2$. Meanwhile, the β -chlorodeceny- λ^3 -bromane by-product, arising from chloride transfer from the solvent to reactive intermediates, could be minimized by using less nucleophilic solvents like CH_3Cl or CCl_4 instead of CH_2Cl_2 . Ochiai and co-workers prepared compound **15** by the ligand exchange of *p*- $\text{F}_3\text{CC}_6\text{H}_4\text{BrF}_2$, on the bromine(III) atom, with potassium cyclopentyltrifluoroborate (5 equiv) in MeCN at low temperature in 61% yield (Scheme 19).^{18a} The resulting bromane does not decompose at room temperature for a short period of time (after 3 days, >92% remains). Complexation of **15** with a crown ether could increase the stability: slow evaporation of a *n*-hexane/ethyl acetate/dichloromethane solution of a 1:2 mixture of **15** and [18]-crown-6 at 4 °C afforded colorless crystals of a 1:1 complex of **15**·[18]crown-6, which were thermally stable and could be left standing under ambient conditions for two weeks. Even though **15** was stable in the solid state, solvolysis took place at room temperature.



Scheme 19 Ochiai and co-workers prepared compound **15** by the ligand exchange of *p*- $\text{F}_3\text{CC}_6\text{H}_4\text{BrF}_2$, on the bromine(III) atom, with potassium cyclopentyltrifluoroborate

Latterly, Ochiai et al. reported the first stereoselective synthesis of (*E*)- β -alkylvinyl(aryl)- λ^3 -bromanes via a boron- λ^3 -bromane exchange reaction (Scheme 20).⁵³ The 1-alkenyl- λ^3 -bromanes with a β -fluoro or β -chloro group were formed through a stereoselective anti-Markovnikov addition of difluoro- λ^3 -bromane to terminal alkynes. For instance, the ligand exchange of Frohn's reagent with (*E*)-1-decenyldifluoroborane (generated in situ from the reaction of potassium decenylborate with $\text{BF}_3 \cdot \text{OEt}_2$) at -78 °C for 1 hour afforded the corresponding (*E*)-vinyl- λ^3 -bromane in 85% yield. A series of vinyl- λ^3 -bromanes could be synthesized in moderate to high yields, but they were thermally labile at ambient temperature and moisture sensitive. However, compound **16** could be stored for several weeks in its solid state at -78 °C. Interestingly, compounds of the type **16** were able to facilitate efficient $\text{S}_\text{N}2$ substitution at a vinylic carbon under mild reaction conditions.

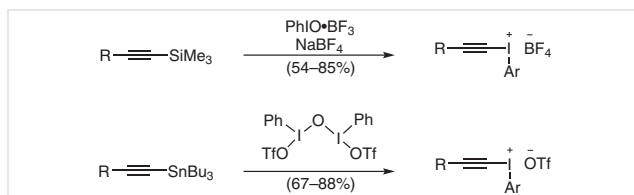


Scheme 20 The first stereoselective synthesis of (*E*)- β -alkylvinyl(aryl)- λ^3 -bromanes

Weakly nucleophilic anions such as HBF_4 , TfOH and Tf_3CH could all function as nucleophiles towards the vinyl- λ^3 -bromanes. For example, the in-plane vinylic $\text{S}_\text{N}2$ substitution of (*E*)-vinyl- λ^3 -bromanes with potassium bis(triflyl)methanide proceeds to give the (*Z*)-vinyloxy oxosulfonium ylides **17** exclusively. Noteworthy, (*E*)- β -alkylvinyl- λ^3 -iodanes failed to undergo similar vinylic $\text{S}_\text{N}2$ reactions with the same weak nucleophiles, which likely signifies the higher nucleofugality of aryl- λ^3 -bromanyl groups in comparison to aryl- λ^3 -iodanyl groups. In general, all of the significant experimental methods for the preparation of alkenyl- λ^3 -bromanes involve difluoro- λ^3 -bromane as the principal reagent. Clearly, these synthetic methods would benefit from the exclusion of fluorinating reagents in order to increase the safety and synthetic convenience for researchers. Nevertheless, the recently conveyed methods are generally high yielding and give rise to sufficiently stable alkenyl- λ^3 -bromanes, such that novel and synthetically valuable procedures could be demonstrated.

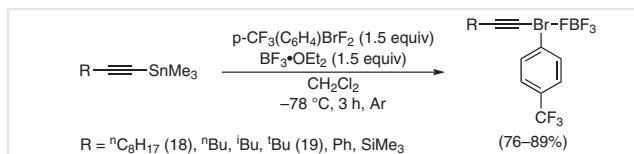
6 Alkynyl- λ^3 -bromanes

The hypervalent 1-alkynyl(aryl)- λ^3 -iodanes exhibit diverse reactivity in modern organic synthesis.⁵⁴ Such compounds are highly electron-deficient owing to the powerful electron-withdrawing nature of the λ^3 -iodanyl groups. They serve as efficient Michael acceptors for a variety of soft nucleophiles. Lewis acid catalyzed ligand exchange processes on iodine(III), of the structure ArIX_2 or ArIX , with boranes, silanes or stannanes, are well-established methods for the syntheses of 1-alkynyl-(aryl)- λ^3 -iodanes (Scheme 21).⁵⁵



Scheme 21 General methods for the synthesis of alkynyl- λ^3 -iodanes

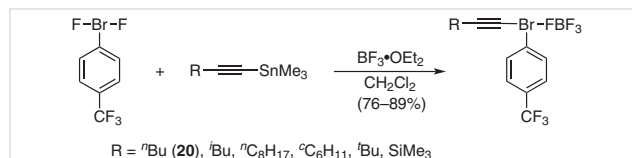
In marked contrast to 1-alkynyl(aryl)- λ^3 -iodanes, the syntheses of 1-alkynyl(aryl)- λ^3 -bromanes is much less orthodox, accredited to the quintessentially more difficult preparation and handling of ArBrX_2 . Although, the reported synthetic procedure is considerably similar to that of λ^3 -iodanes. Until recently, hypervalent 1-alkynyl(aryl)- λ^3 -bromanes had not been synthesized or characterized. In 2003, Ochiai, Frohn, and co-workers reported the first synthesis of alkynyl- λ^3 -bromanes via the Lewis acid catalyzed stannane–bromine(III) exchange of difluoro[*p*-(trifluoromethyl)phenyl]- λ^3 -bromane with 1-alkynylstannanes (Scheme 22).⁵⁴ The ligand exchange with silanes instead of stannanes gave poor results under the same conditions, but 1-alkynyl(trifluoromethyl)borates could also be used to access the desired bromanes. Difluoro- λ^3 -bromane was prepared in 72% yield by reacting *p*-trifluoromethylphenyl(trimethyl)silane with bromine trifluoride at -78 to -25 °C in dichloromethane. Subsequently, the reaction of difluoro- λ^3 -bromane with a trimethylstannyl derivative and $\text{BF}_3\cdot\text{OEt}_2$ at -78 °C afforded the alkynylbromane **18** in 82% yield.



Scheme 22 The first synthesis of alkynyl- λ^3 -bromanes

In this reaction, an excess amount of difluorobromane (1.5 equiv) was required. Selective stannane–Br(III) exchange could be achieved with various primary, secondary, and tertiary alkylethynyl stannanes in good yields (76–89%). However, the ligand exchange with phenylethynyl stannane was not successful and gave a tarry matter. Contamination of these oily λ^3 -bromanes with a small amount

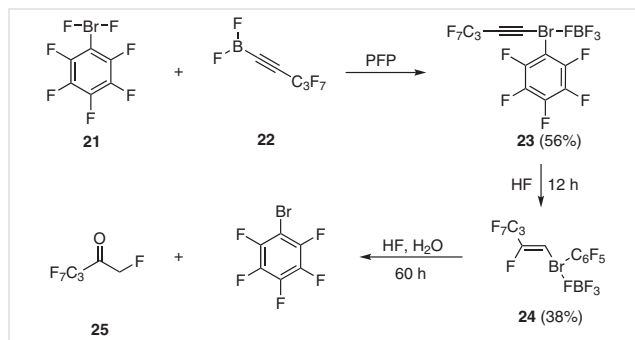
(4–9%) of (*E*)- β -fluorovinyl- λ^3 -bromanes was noted in every case. Furthermore, due to their high Michael-accepting ability, these bromanes were relatively labile and gradually decomposed to give *p*-bromo(trifluoromethyl)benzene upon standing at room temperature. However, they could be handled under air for brief moments at a time. The bromanes were also highly water sensitive: the half-life ($t_{1/2}$) of **18** in CDCl_3 was decreased from 13 days to just 25 minutes in the presence of a small amount of water. Despite this, full structural conformation of the prepared bromanes was still possible by the complexation of **19** with a crown ether. The slow evaporation of a dichloromethane/diethyl ether (1:1) solution of a 2:1 mixture of λ^3 -bromane **19** and [18]-crown-6 at 4 °C under argon afforded colorless single crystals of a 2:1 complex that was suitable for X-ray crystallography. Complexation of λ^3 -bromanes with crown ethers seems to be a valuable technique for stabilizing such structures of this type and has been reported since. As expected, the strong electron-withdrawing nature of the phenyl- λ^3 -bromanyl moiety combined with the long C–C triple bond length made these alkynyl bromanes highly efficient Michael acceptors. The compounds underwent tandem Michael–carbene rearrangement in the presence of a variety of nucleophiles under mild conditions. For instance, exposing compound **18** to Bu_4OTf in dichloromethane at room temperature afforded the alkynyl tosylate in 55% yield, alongside the cyclic alkenyl tosylate as a minor product (5% yield). In fact, weakly nucleophilic superacid conjugate bases could also participate as a Michael donor, which cannot be observed in iodine chemistry. Attack of the β -acetylenic carbon of **18** by a sulfonate anion generated the alkylidene carbene. A variation of this procedure using alkynyl stannanes as nucleophiles can be used to product polyynes.⁵⁶ More recently, Frohn and co-workers accessed alkynyl-(aryl)- and bis(alkynyl)- λ^3 -bromonium salts starting from aryl difluoro bromanes (Scheme 23).^{21,57} Firstly, alkynyl-(aryl)bromonium tetrafluoroborates could be obtained in excellent yields by the reaction of $p\text{-F}_3\text{CC}_6\text{H}_4\text{BrF}_2$ with alkynyltrimethyl stannanes bearing electron-rich alkynyl groups under acidic conditions at -70 °C.



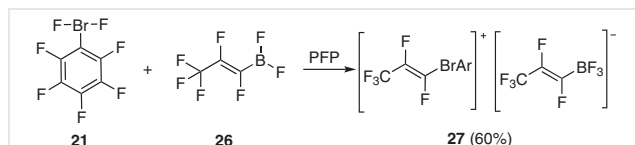
Scheme 23 Alkynyl(aryl)bromonium salts accessed by Frohn

Under similar conditions, the authors were able to access the previously unknown perfluorinated alkynyl(aryl)bromonium versions by boron–bromine(III) exchange, in this case using the electron-deficient $\text{C}_6\text{F}_5\text{BrF}_2$ hypervalent bromine source in place of $p\text{-F}_3\text{CC}_6\text{H}_4\text{BrF}_2$ (Scheme 24). For instance, the perfluorinated molecule **23** was obtained by addition of **22** to a cold solution of bro-

mane **21** in 1,1,1,3,3-pentafluorobutane (PFP), and was isolated as a reasonably stable white solid after removal of all volatiles. In the same fashion, the reaction of *trans*-pentafluoroprop-1-en-1-yl(difluoro)borane (**26**) with the same bromane (**21**) yielded the perfluorinated product **27** with retention of configuration (Scheme 25). Interestingly, this retained configuration is different from the synthesis of $[(\text{CF}_3\text{CF}=\text{CF})_2\text{Br}][\text{CF}_3\text{CF}=\text{CFBF}_3]$ by the reaction of a borane and BrF_3 , where partial conversion into the *cis*-isomer transpires.²¹ Transformation of the polarizable triple bond in the perfluoroalkynyl moiety, bonded to bromine(III), was possible due to the highly electron-deficient property of the C–C triple bonds. Upon slow addition of weakly nucleophilic hydrogen fluoride at 24 °C to **23**, a 38% yield of **24** was obtained after 12 hours. Extension of the reaction time to 60 hours resulted in the isolation of bromopentafluorobenzene and 1*H*,1*H*-octafluoropentan-2-one (**25**), likely caused by the presence of trace amounts of water. Formation of the ketone indicates the enhanced electrophilicity of the perfluoroalkynyl- λ^3 -bromanes. Despite the proficiency of the methods for the synthesis of alkynyl- λ^3 -bromanes, they do not comply with contemporary demands for safe and accessible procedures that are required for the widespread utilization of these compounds. In essence, the prerequisite for fluorinating reagents remains prevalent in all methods, including modern-day literature. Certainly, methodology that can avoid the necessary ligand exchange of ArBF_2 , that are typically troublesome to handle, would improve the expediency of such synthetic techniques.



Scheme 24 The previously unknown perfluorinated alkynyl(aryl)-bromonium salts accessed by boron–Br(III) exchange



Scheme 25 Br(III) exchange with *trans*-boranes

7 Conclusion and Prospects

Unlike hypervalent organo- λ^3 -iodanes, the chemistry of λ^3 -bromanes is greatly underdeveloped despite their synthesis being known since 1952. This can be attributed to the limitations in user-friendly synthetic methods for their syntheses, as well as their lack of stability. Consequently, their reactivity profile is largely under-explored in terms of synthetic application. Overall, the progress in the field of hypervalent bromine chemistry is surprisingly slow compared to the rapid growth of hypervalent iodine chemistry. However, the recent breakthroughs reported in this year (2021) certainly simplify the synthesis techniques significantly, and as such improve the accessibility of different hypervalent bromine compounds. We believe this will be pivotal in unfolding their unique reactivities and attracting more research groups to explore the largely uncharted field of hypervalent bromine compounds.

Conflict of Interest

The authors declare no conflict of interest.

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