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FULL PAPER

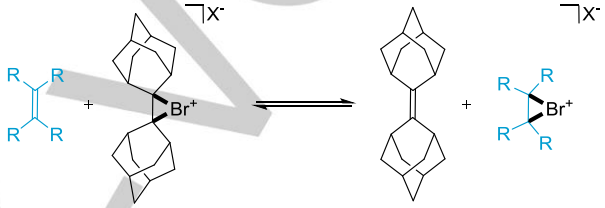
Stable Bromiranium Ions with Weakly-Coordinating Counterions as Efficient Electrophilic Brominating Agents

Christoph Ascheberg,[a] Jonathan Bock,[a] Florenz Buß,[b] Christian Mück-Lichtenfeld,[a] Constantin G. Daniliuc,[a] Klaus Bergander,[a] Fabian Dielmann[b] and Ulrich Hennecke*[a]

Abstract: Electrophilic halogenating agents are an important class of reagents in chemical synthesis. Herein, we show that sterically demanding bromiranium ions with weakly coordinating counterions are highly reactive electrophilic brominating agents. Despite their high reactivity these reagents are stable, in one case even under ambient conditions and can be applied in electrophilic halogenations of alkenes as well as heteroatoms.

Introduction

The electrophilic halogenation of alkenes is one of the fundamental reaction classes of organic chemistry. Dihalogenation, halolactonisation and other halo-functionalisations are important synthetic methods and have often been applied in total synthesis.[1] In general, it is assumed that these reactions take place via the formation of a cyclic, cationic intermediate, a haliranium ion, which nicely explains the usually observed *anti*-addition towards the alkene.[2,3] The existence of halonium ions and more specifically haliranium ions in solution was demonstrated by Olah using NMR spectroscopy.[4] Based on evidence from NMR spectroscopic investigations and theoretical calculations the haliranium structure seems to be preferred over β-halocarbenium ion structures in solution, however, this might not be true in all cases.[5] The first stable haliranium ion was obtained by bromination of the sterically highly demanding alkene adamantylidene adamantane by Wynberg.[6] This bromiranium ion **2-Br$_3$** was formed as a rather insoluble tribromide salt. Definite prove of the cyclic nature of this ion in the solid state was provided by Brown through X-ray structure analysis.[7] Later on, the triflate salt of **2-OTf** was prepared and proved to be an useful tool for mechanistic studies of electrophilic alkene brominations.[8] The bromiranium ion **2-OTf** can directly transfer the electrophilic bromine atom to another alkene, a process called alkene-to-alkene transfer of bromiranium ions (Scheme 1).[8,9] This direct transfer via an associative mechanism enabled the use of **2-OTf** as an electrophilic halogenating agent in mechanistic investigations of halocyclizations reactions.[10] Furthermore, the use of chiral bromiranium ions as chiral halogenating agents has been proposed.[11] However, from a synthetic perspective, there does not seem to be an advantage in using haliranium ions as halogenating agents in halocycloetherifications or halolactonisations. Standard electrophilic halogenating agents such as elemental halogens or *N*-haloamides are reactive enough for this type of transformations and clearly more atom-economic.



X = Br_3^-: **2-Br$_3$**
X = OTf^-: **2-OTf**
X = $BArF^-$: **2-BArF**
X = $Al_2Br_7^-$: **2-Al$_2$Br$_7$**

Scheme 1. Bromiranium ions and their alkene-to-alkene transfer.

The situation could be different in reactions, which require highly reactive halogenating agents such as halogen-induced polyene cyclizations.[12] *N*-Haloamides and many other halogenating agents lack sufficient reactivity to induce high-yielding polyene cyclizations. The use of elemental bromine leads usually only to dibromides as the bromide anion is too nucleophilic to allow further cyclizations after the initial electrophilic bromination. Barluenga showed that his reagent provides good yields for monocyclizations, but examples with this reagent for polycyclizations are missing.[13] The importance of the counterion in these cyclizations was shown by Snyder, who developed $BrS(Et)_2^+$ $SbCl_5Br^-$ (BDSB) as highly reactive halogenating agent.[14,15] Alternatively, catalytic approaches for the activation of *N*-haloimides are known, which allow even enantioselective halogen-induced polyene cyclizations, however, under those reaction conditions partially cyclized side products are produced and a second cyclization step is required to achieve good cyclization yields.[16]

With these facts in mind, we set out to prepare bromiranium ion salts with weakly-coordinating counterions as possible highly reactive brominating agents. It could be demonstrated that such ions with either tetrakis[3,5-bis(trifluoromethyl)phenyl] borate ($BArF^-$) or $Al_2Br_7^-$ counterions are easily prepared on gram scale. Furthermore, those new salts proved to be highly reactive halogenating agents allowing efficient polyene-type cyclizations as well as the halogenation of heteroatoms.

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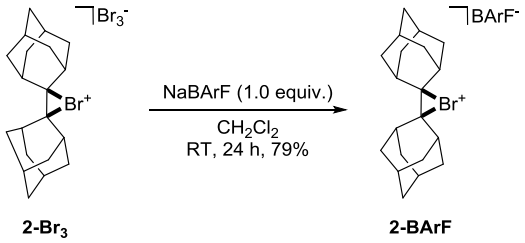
Results and Discussion

Synthesis of Bromiranium Ion Salts with Weakly-Coordinating Anions

Originally, the bromiranium ion of adamantylidene adamantane (**1**) was prepared as the tribromide salt **2-Br$_3$**.[6] However, due to the presence of the tribromide, which can release bromine and a nucleophilic bromide ion, this is not a very useful brominating agent. Instead, Brown prepared the triflate salt **2-OTf**, but also the triflate interacts with the bromiranium ion.[8] The solid state structure shows a clear contact between the bromine atom and one of the oxygen atoms of the triflate ion (O···Br distances of 294.2 or 308.1 pm for the two independent ions in the unit cell, respectively). Furthermore, the triflate is still nucleophilic and **2-OTf** reacts with cyclohexene to give 2-bromocyclohexyl triflate.[10]



Scheme 2. Synthesis of the stable bromiranium salt **2-BArF**.

To obtain a bromiranium salt with a weakly-coordinating anion we chose to prepare the salt **2-BArF**. This salt has been used previously as a halogenating agent for an osmium carbonyl complex, but no procedure for its preparation or data on its reactivity have been reported.[14] For its preparation we used a salt metathesis reaction with sodium tetrakis[3,5-bis(trifluoromethyl)-phenyl] borate (NaBArF). The stoichiometric addition of NaBArF to **2-Br$_3$** in dichloromethane at room temperature formed **2-BArF** (Scheme 2). The reaction was allowed to stir overnight and sodium bromide and Br_2 as byproducts were removed by filtration and evaporation, respectively. The crude product could be purified by crystallization from dichloromethane/hexane at -20 °C. **2-BArF** precipitates as pale yellow crystals in 79% yield. The reagent is stable at room temperature and, at least briefly, under air. Nevertheless, it is recommended to store **2-BArF** protected from light and air at low temperature to prevent decomposition. The ^{13}C-NMR spectrum shows five resonances for the adamantyl moiety, which suggests that rapid exchange of the bromenium, similar to **2-OTf**, takes place, possibly via alkene-to-alkene transfer.[8] This process is operative even at -78°C (see supporting information for NMR spectra at -78 °C).

The crystals obtained of **2-BArF** allowed the determination of its solid state structure using X-ray crystallography (Figure 1). Overall the solid state structure of the bromiranium ion of **2-BArF** is similar to the previous determined structures in **2-Br$_3$** and **2-OTf**. Small differences can be observed in the length of the C-Br bonds, which are slightly longer and more symmetrical in **2-BArF** (214.9(4) pm and 213.4(4) pm) compared to **2-Br$_3$** (211.6(6) pm and 219.4(6) pm) and **2-OTf** (211.8(10) pm and 213.6(10) pm or 208.9(10) pm and 211.4(20) pm for the two independent ions in the unit cell, respectively). The main difference is the only very weak interaction with the counterion in the structure of **2-BArF**. The shortest inter-ion contact of the bromine atom is observed to two carbon atoms of one of the aryl rings in the BArF anion with C···Br distances of 357.0 and 367.4 pm being at the sum of their van der Waals radii (360 pm).[18] This is quite different to **2-Br$_3$** and **2-OTf**, which show rather short Br···Br (309.6 pm) in **2-Br$_3$** or O···Br (294.2 and 308.1 pm for the two independent ions in the unit cell) contacts, respectively. This suggests that the reactivity of **2-BArF** is close to an ideal, uncoordinated bromiranium ion.

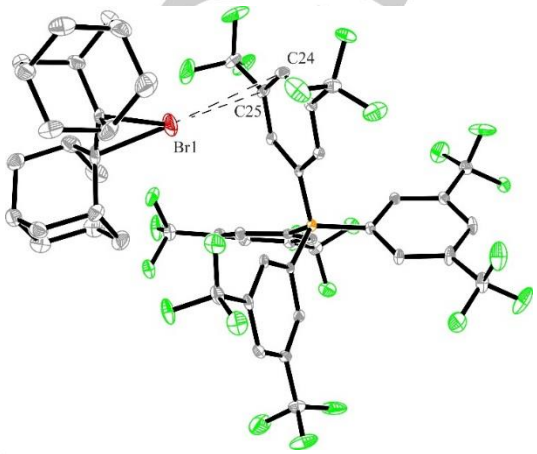
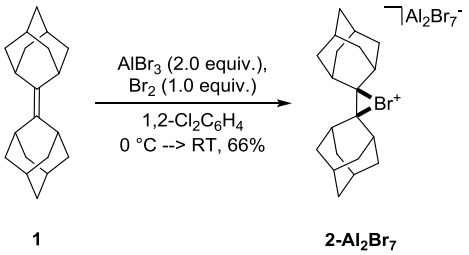


Figure 1. Solid-state structure of **2-BArF**. Thermal ellipsoids are shown with 30% probability. Hydrogen atoms have been omitted for clarity.

Although **2-BArF** is an easy-to-handle brominating agent, the BArF anion is not ideal if atom-economy is concerned. As an alternative pure inorganic anions were investigated. Attempts to brominate **1** with a combination of Br_2 and $SbCl_5$ did not provide a pure product. Instead, we tried a direct route to form the bromiranium ion by using Br_2 and $AlBr_3$. Expecting the formation of the $Al_2Br_7^-$-anion,[19] a combination of one equivalent of Br_2 and two equivalents of $AlBr_3$ were employed for the halogenation of **1** (Scheme 3). The use of 1,2-dichlorobenzene as solvent was crucial as dichloromethane proved to be not stable under the reaction conditions. After the addition of pentane to the reaction mixture, the product **2-Al$_2$Br$_7$** crystallized at -20 °C as yellow solid in 66% yield. In contrast to **2-BArF** the NMR spectrum of **2-Al$_2$Br$_7$** did not show any dynamic effects and all expected signals could be identified. Again, in contrast to **2-BArF** this bromiranium salt is not stable under ambient conditions. Under air, we could observe decomposition with production of white smoke. Considering that **2-BArF** is stable, most likely decomposition/hydrolysis of the $Al_2Br_7^-$ anion is responsible for this behavior.



Scheme 3. Synthesis of the bromiranium salt **2-Al$_2$Br$_7$**.

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The crystals obtained from the bromiranium salt **2-Al$_2$Br$_7$** were suitable for an X-ray crystal structure analysis (Figure 2). The C···Br distances in the solid-state structures of the two independent bromiranium ions found in the unit cell are again quite similar to the previous structures with symmetrical bromiranium ions (212.6(13) pm and 215.8(14) pm or 212.9(14) pm and 213.7(15) pm for the two independent ions in the unit cell, respectively). The Br···Br distances between the positively polarized bromine atom of the bromiranium ion and the negatively polarized bromine atoms of the anion (356.3 pm) are below the sum of their van der Waals radii (380 pm[18]), but significantly longer than the Br···Br distance in **2-Br$_3$** (309.6 pm), indicating a much weaker interaction between the anions and the bromiranium cations.

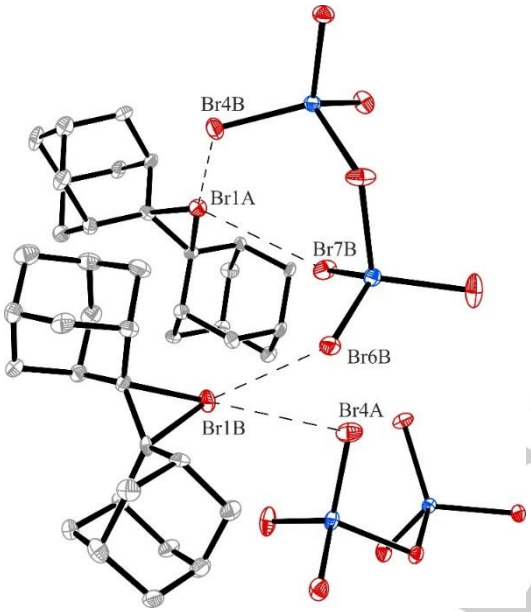
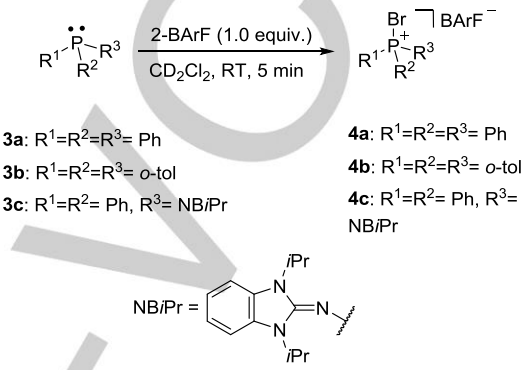


Figure 2. Solid-state structure of **2-Al$_2$Br$_7$**. Thermal ellipsoids are shown with 30% probability. Hydrogen atoms have been omitted for clarity.

Bromiranium ions as Brominating agents for heteroatoms

To explore the potential of **2-BArF** as bromenium ion transfer agent towards heteroatoms, we investigated the reactivity of **2-BArF** with phosphines comprising different stereoelectronic properties. Therefore, PPh_3 (**3a**), P(*o*-tol)$_3$ (**3b**), P(NB*i*Pr)Ph$_2$ (**3c**) and P(C$_6$F$_5$)$_3$ (**3d**) were included in our study (Scheme 4). The decoration of phosphines with strong π-donor groups such as the benzimidazolin-2-ylidenamino (NB*i*Pr) substituent has been shown to give particularly electron rich phosphines.[20] The stoichiometric reaction of **2-BArF** with phosphines **3a-d** was investigated via reactions in NMR tubes. The NMR analysis indicated the clean and quantitative formation of the bromophosphonium salts [(*o*-tol)$_3$PBr]$^+$ [BArF]$^-$ (**4a**), [Ph$_3$PBr]$^+$ [BArF]$^-$ (**4b**) and [(NB*i*Pr)Ph$_2$PBr]$^+$ [BArF]$^-$ (**4c**), respectively. The ^{31}P-NMR signals of **4a** (52.9 ppm) and **4b** (46.4 ppm) are shifted downfield compared to those of the corresponding phosphines, while the ^{31}P-NMR signal of **4c** (16.8 ppm) appears at higher field compared to that of P(NB*i*Pr)Ph$_2$ (33.7 ppm). The reaction of **2-BArF** with **3d**, a very electron-deficient phosphine, showed significantly different behavior. The corresponding bromophosphonium salt **4d** was formed only in about 20% in the stoichiometric reaction indicating a similar bromenium ion affinity of **1** and **3d**. Interestingly, this study indicates that the reaction of **2-BArF** with phosphines can be used as a general protocol for the direct synthesis of bromophosphonium salts containing a weakly coordinating anion as long as the phosphine is more electron rich than phosphine **3d**.[21]



Scheme 4. Bromination of phosphines using **2-BArF**.

In a second set of experiments, the reactivity of **2-BArF** towards diethyl sulfide (**5**) was investigated. This was carried out to compare the reactivity of **2-BArF** with BDSB, which is a bromodiethyl sulfonium salt.[14] However, treatment of **2-BArF** in dichloromethane with one equivalent of diethyl sulfide in a NMR tube provided a surprising result. The ^{1}H- and ^{13}C-NMR spectra showed only one set of signals (Figure 3, C), which were neither identical to the starting materials (Figure 3, A and B) nor to adamantylidene adamantane, which speaks against the formation of a free bromodiethyl sulfonium ion.

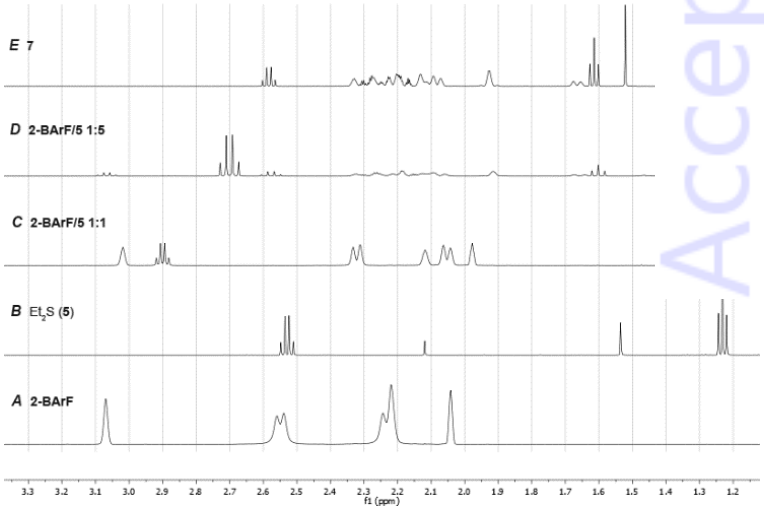


Figure 3. Stacked ^{1}H-NMR spectra of **2-BArF** (A), SEt$_2$ (**5**, B), **2-BArF/5**: 1/1 (C), **2-BArF/5**: 1/5 (D) and **7** (E).

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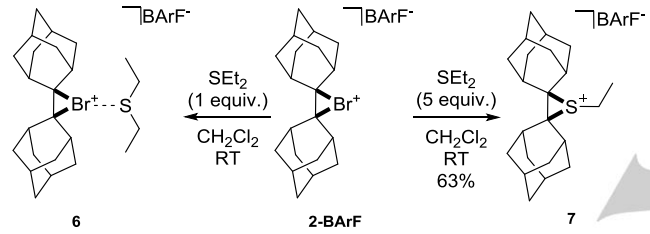
All signals underwent significant shifts compared to the starting materials and some signals such as the ^{13}C-NMR signals of C1 of the adamantylidene groups and the CH_2-groups of diethyl sulfide became very broad. For example, the CH_2-group of diethyl sulfide, which resonates at 2.53 ppm in CH_2Cl_2 (spectrum A) was shifted to 2.90 ppm (spectrum C) upon **2-BArF** addition. A possible explanation is the coordination of **5** towards the bromine of the bromiranium ion without release of a bromo sulfonium ion into the solution (Scheme 5). Such a coordination of a Lewis base towards a haloiranium can be found in the solid state structure of the iodiranium ion of **1**, which contains a coordinated water molecule.[8b] DFT calculations suggest that an adduct such as **6** can be stable (see supporting information for details). Attempts to identify adduct **6** by mass spectrometry were not successful. The ESI-MS spectrum of the **2-BArF/5** 1:1 mixture in CD_2Cl_2 solution showed an intensive signal at 329.2315, which corresponds to the ethyl thiiranium ion of adamantylidene adamantane (**7**, Scheme 5), and a less intense signal corresponding to the bromodiethyl sulfonium ion. Furthermore, based on the broad NMR signals indicating a dynamic process, it cannot be excluded that several, rapidly equilibrating compounds are present.



6 2-BArF 7

Scheme 5. Reaction of **2-BArF** with diethyl sulfide (**5**).

In further investigations, **2-BArF** was treated with an excess of five (for NMR experiments) or ten equivalents (for crystallization experiments) of diethyl sulfide. The NMR spectra with excess **5** show signals for three different ethyl groups (Figure 3, D), one at 3.07 ppm, one very intense signal at 2.70 and one at 2.58 ppm. The most intense signal, which should belong to the excess diethyl sulfide was still shifted compared to pure diethyl sulfide. A second ethyl group was identified to belong to the thiiranium ion **7**, which was formed in almost quantitative yield under these conditions. The identity of the third ethyl group signal is not fully clear, but its chemical shifts are significantly different from ethyl bromide, while being similar to literature data for triethyl sulfonium triflate.[22]

On a preparative scale, **7** could be obtained as crystalline solid in 63% yield simply by mixing **2-BArF** in dichloromethane with ten equivalents of **5** followed by vapor diffusion of pentane into the mixture (Scheme 5). A single crystal was analyzed by an X-ray diffraction study that confirmed the structure of **7** to be the ethyl thiiranium ion (Figure 4). Bond length and angles in the solid-state structure of **7** are very similar to values previously observed for the corresponding *S*-phenyl thiiranium ion of adamantylidene adamantane.[23]

When **2-BArF** was treated with one equivalent of tetrahydrothiophene or one equivalent of dibutylselenide, similar behavior than with diethyl sulfide was observed. The CH_2-groups next to the sulfur/selenium atom showed very significant shifts in the proton NMR and some proton and ^{13}C-NMR signals became broad indicating dynamic behavior (see supporting information for NMR spectra). However, in these cases the addition of an excess of sulfide/selenide did not lead to the appearance of more than one set of NMR signals and the NMR spectra remained dynamic. Attempts to crystallize the reaction products have not been successful so far, but in the case of the reaction of **2-BArF** with an excess (five equivalents) dibutyl selenide ESI-MS spectra show a signal with m/z 405.2065 corresponding to a butyl seleniranium ion ($C_{24}H_{37}Se$).

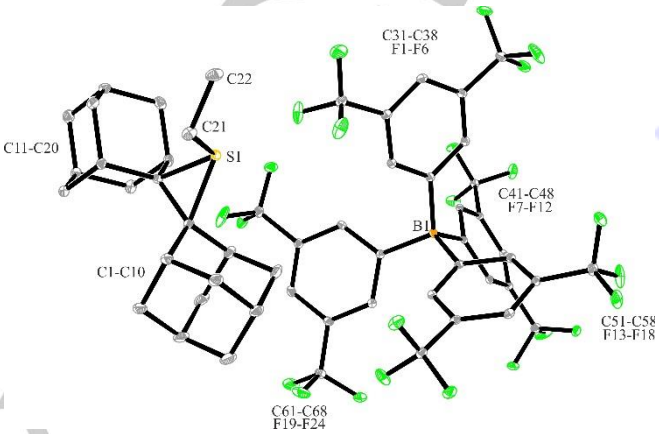


Figure 4. Solid state structure of ethylthiiranium ion **7**. Thermal ellipsoids are shown with 30% probability. Hydrogen atoms have been omitted for clarity.

The mechanism of formation of **7** out of **2-BArF** and **5** is currently not clear. One possibility would be that a bromodiethyl sulfonium ion is released by the reaction of **2-BArF** and **5**, which could subsequently react with excess **5** to give ethylsulfenyl bromide and a triethylsulfonium ion. Sulfenylation of **1** by ethylsulfenyl bromide would then provide **7** (Scheme S1 in the supporting information).

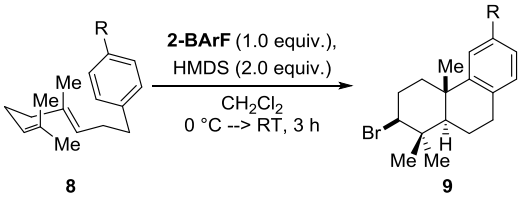
Bromiranium-induced polyene cyclizations

To investigate the potential of **2-BArF** as brominating agent in organic synthesis, several examples of bromiranium-induced polyene cyclizations were investigated (Table 1). Initial investigations were conducted on homogeranyl benzene **8a**.[12i, 14] This substrate has been investigated previously, and using conventional electrophilic halogenating agents such as NBS or TBCO only low yields of tricyclic products are obtained and main products are either simple addition products without cyclization or, especially in methods employing a Lewis basic promoter or catalyst, monocyclization products.[12,14,16] This makes an additional, Brønstedt acid-catalyzed cyclization necessary to reach tricyclic product **9a**.[12i, 16] Good yields of **9a** can be obtained directly by using BDSB, however, this requires the use of nitromethane as solvent.[14]

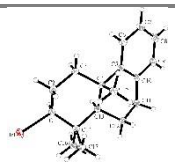
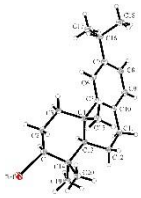
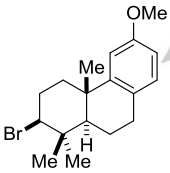
When homogeranyl benzene **8a** was treated with **2-BArF** in dichloromethane without the addition of a base, the desired cyclization product **9a** was only obtained in varying, but generally low quantities. Instead, the proton-induced cyclization product **10** proved to be the main component of the reaction mixture. Its formation was attributed to the *in situ* formation of the super acid

HBArF (or, more likely, its aryl ring adduct) in the last step of the bromocyclization, a S_EAr reaction (see supporting information for a likely mechanism, Scheme S2).

Table 1. Cyclization of homogeranyl benzenes **8** using **2-BArF** as brominating agent.[a]

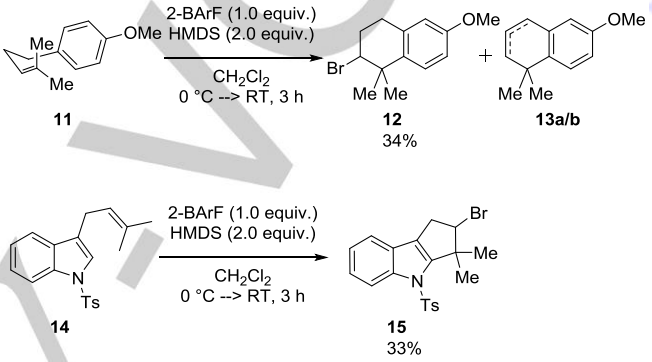


8 **9**

Entry	Starting material	Product	Yield (%)
1	**8a** (R=H)	 **9a**	64[b] (26)[c]
2	**8b** (R=*i*Pr)	 **9b**	29[d]
3	**8c** (R=OMe)	 **9c**	50[b] (30)[c]

[a] **8** (0.4 mmol) and HMDS (0.8 mmol) in CH_2Cl_2 (0.13 M) were treated with **2-BArF** (0.4 mmol) at 0 °C for 3 h. [b] Yield after column chromatography to give products of about 90% purity. [c] In brackets: yield after crystallization from acetone. [d] Isolated yield after column chromatography.

To prevent this proton-induced cyclization, a bulky base was added to the bromocyclization. 2,6-Di(*t*butyl)-4-methyl pyridine or hexamethyldisilazane (HMDS) worked equally well and enabled efficient bromocyclization reactions. The main product was now indeed the fully cyclized **9a**. However, it was accompanied by small amounts of a complex mixture of minor byproducts. Purification by column chromatography enabled the isolation of the main cyclization product **9a** with about 90% purity in good yield of 64% (Table 1, entry 1). The isolation of highly pure **9a** was possible by crystallization from acetone, however, this was accompanied by a significant loss of yield (26% after crystallization). The relative configuration of **9a** could be established by X-ray structure analysis. The observed configuration of **9a** could result from a chair-chair-type transition state according to the Stork-Eschenmoser hypothesis.[24] Cyclization of homogeranyl benzenes with substituents on the aromatic ring such as an isopropyl group (**8b**) or a methoxy group (**8c**) provided similar results. Starting material **8b** with an isopropyl-substituent provided tricyclic **9b** as the main product, but isolation in high purity required a lengthy column chromatography to give **9b** in moderate 29% yield (Table 1, entry 2). Crystallization of the product from pentane was possible and a resulting crystal could be analyzed by X-ray diffraction. The solid state structure of **9b** showed relative stereochemistry identical to **9a**. Starting material **8c** provided product **9c** with about 90% purity in acceptable yield (49%, Table 1, entry 3). Again, crystallization from acetone led to pure product in lower overall yield (30%).[25]



Scheme 6. 2-BArF-induced cyclization of prenylated anisole **11** and *N*-tosyl indole **14**.

2-BarF was also used to cyclize alkenyl-substituted aromatics. Following the standard procedure, alkene **11** was reacted to give **12** as the main product in 34% yield (Scheme 6). The relatively low yield is caused by the sensitivity of the product **12** to the elimination of HBr under the reaction conditions. The corresponding elimination products **13a/b** could be observed by GC-MS, however, isolation in pure form proved to be difficult. Similarly, indole **14** carrying a prenyl side chain in the 3-position was cyclized to give cyclopentindole 15. When 1.0 equivalent of **2-BarF** was used under standard conditions, about 60% conversion was observed and the product could be isolated in 33% yield.

Conclusions

The results show that stable bromiranium ions based on adamantylidene adamantane with weakly-coordinating counterions can be easily obtained by anion exchange from known **2-Br$_3$** or by direct synthesis. Bromiranium salt **2-BArF** comprising the tetrakis(3,5-bistrifluoromethylphenyl) borate anion shows high reactivity as an halogenating agent for the halogenation of heteroatoms as well as of unsaturated hydrocarbons. The experiments with **2-BArF** as halogenating agent for heteroatoms show that this type of reagent does not only act as halogenating agent for alkenes via alkene-to-alkene transfer, but does directly react with more or less Lewis-basic heteroatoms. Therefore, this halogenating agent could be of high

interest in element organic chemistry, where it could provide a cationic bromine atom ion combined with a weakly-coordinating counterion and a sterically very demanding (and therefore not very reactive) alkene as the only side product.

As a halogenating agent in organic chemistry, **2-BArF** shows how important a weakly-nucleophilic counterion for polyene-type cyclizations is. Whereas most other halogenating agents are not capable to induce double cyclization of homogeranyl benzene, with **2-BArF** the tricyclic product is obtained with good efficiency. In contrast to BDSB, this is already the case with dichloromethane as solvent and no polar solvent such as nitromethane is necessary to increase reactivity or solubility.

Experimental Section

General Methods: All manipulations involving air- or moisture-sensitive reagents or intermediates were carried out in dried glassware under argon and performed by using standard Schlenk and drybox techniques. Dry and oxygen-free solvents were employed for reactions. Solvents for extraction and flash chromatography were distilled before use. Commercial compounds were purchased by standard suppliers (ABCR, Acros, Alfa Aesar, Sigma-Aldrich or TCI) and used without further purification. Flash chromatography (FC) was carried out on silica gel 60 (40-63 µm) under argon pressure (approximately 1.1-1.5 bar). IR spectra were recorded with a Digilab FTS 4000 with an attenuated total reflectance (ATR) unit. The NMR spectroscopic data were recorded on a Bruker DPX-300, Agilent DD2 600, Bruker AVANCE I 400, Bruker AVANCE III 400 or Bruker AVANCE II 200 spectrometer. Chemical shifts (δ) are reported in ppm relative to $SiMe_4$ (^1H, ^{13}C), 85% H_3PO_4 (^{31}P) and referenced to either the residual solvent signal for ^1H-NMR or the solvent signal for ^{13}C-NMR (δ = 7.26/77.2 ppm for $CDCl_3$; δ = 5.32/54.0 ppm for CD_2Cl_2) or internally by the instrument after locking and shimming to the deuterated solvent (^{11}B, ^{19}F, ^{31}P). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad signal. Mass spectra with electrospray ionization (MS-ESI-EM, m/z) were recorded on a Bruker MicroTof or a Thermo Scientific Orbitrap LTQ XL (Nanospray). (*E*)-3,7-Dimethylocta-2,6-diene-1-yldiethylphosphate[20], P(NB*i*Pr)Ph_2[16a] (**3c**), homogeranyl benzene[20] (**8a**) and 1-methoxy-4-homogeranyl benzene[12a] (**8c**) were prepared following literature procedures.

(*E*)-1-(4',8'-dimethylnona-3',7'-diene-1'-yl)-4-isopropylbenzene (8b): Magnesium turnings (1.09 g, 45.0 mmol, 1.50 equiv.) were placed in a Schlenk-flask, THF (30 mL) was added and the suspension was cooled to 0 °C. 4-Isopropylbenzyl chloride (4.95 mL, 30.0 mmol, 1.00 equiv.) in THF (40 mL) was added dropwise. After warming to RT the reaction mixture was stirred for 1 h. The reaction mixture was now slowly added to a precooled solution of (*E*)-3,7-dimethylocta-2,6-diene-1-yldiethylphosphate (4.35 g, 15.0 mmol, 1.00 equiv.) in THF (40 mL) at -45 °C. The reaction mixture was allowed to warm up RT and stirred overnight. After addition of NH_4Cl (*aq.*, *sat.*) and H_2O the mixture was stirred for 10 min. The aqueous phase was extracted with EtOAc:pentane 1:2 (3x75 mL) and the combined organic phases were washed with $NaHCO_3$ (*aq.*, *sat.*) and NaCl (*aq.*, *sat.*) and dried over $MgSO_4$. Purification of the crude product by column chromatography (cyclohexane) provided the product as a colorless oil (2.41 g, 8.91 mmol, 59 %). **IR (film):** 2960, 2923, 1513, 1449, 1382, 1108, 1056, 984, 822, 631, 549, 532, 511, 509. **^{1}H-NMR** (400 MHz, $CDCl_3$, 295 K): δ = 7.17-7.11 (m, 4H), 5.23-5.17 (m, 1H), 5.13-5.07 (m, 1H), 2.88 (sept, ^3J = 6.9 Hz, 1H), 2.65-2.57 (m, 2H), 2.34-2.25 (m, 2H), 2.11-2.03 (m, 2H), 2.02-1.95 (m, 2H), 1.69 (d, ^3J = 0.9 Hz, 3H), 1.61 (s, 3H), 1.57 (s, 3H), 1.25 (d, ^3J = 6.9 Hz, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$, 295 K): δ = 146.3, 139.9, 135.8, 131.5, 128.5, 126.4, 124.5, 123.9, 39.9, 35.9, 33.8, 30.2, 26.9, 25.9, 24.2, 17.8, 16.1. **MS-ESI-EM** (with added $AgCO_2CF_3$): *m/z* = 377.1393 calculated for $C_{20}H_{30}Ag^+$ ([M+Ag]$^+$), found: 377.1398.

1-Methoxy-4-(4-methylpent-3-en-1-yl)benzene (11): Magnesium turnings (0.73 g, 30.0 mmol, 1.50 equiv.) were placed in a Schlenk-flask and Et_2O (15 mL) and THF (15 mL) were added. The suspension was cooled to 0 °C and 4-methoxybenzyl chloride (4.95 mL, 30.0 mmol, 1.0 equiv.) in a Et_2O (15 mL)/THF (15 mL) mixture was added dropwise. After warming to RT the reaction mixture was stirred for 1 h. The reaction mixture was now slowly added to a precooled solution of 1-bromo-3-methyl-2-butene (1.20 mL, 10.0 mmol, 1.0 equiv.) in THF (30 mL) at -78 °C and the resulting mixture was stirred at -78 °C for 1 h. The mixture was allowed to warm to RT and stirred overnight. Saturated aqueous NH_4Cl-solution was added and the mixture was stirred for 10 min. The mixture was extracted three times with CH_2Cl_2, the combined organic phases were washed with saturated aqueous $NaHCO_3$-solution and brine and dried over magnesium sulfate. The crude product was purified by column chromatography (pentane) followed by warming to 60 °C for 3 h *in vacuo* (to remove 3-OMe toluene) to provide the product (0.96 g, 5.05 mmol, 51 %) as a colourless liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$, 296 K): δ = 7.25 (m, 1H, Ar-H), 6.87-6.76 (m, 3H), 5.27-5.20 (m, 1H), 3.84 (s, 3H), 2.70-2.64 (m, 2H), 2.42-2.29 (m, 2H), 1.75 (s, 3H), 1.64 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$, 296 K): δ = 159.7, 144.2, 132.2, 129.3, 123.9, 121.0, 114.3, 111.1, 55.2, 36.3, 30.1, 25.8, 17.8. **MS-ESI-EM** (with added $AgCO_2CF_3$): *m/z* = 297.0405 calculated for $C_{13}H_{18}OAg^+$ ([M+Ag]$^+$), found: 297.0405.

***N*-Tosyl-3-prenylindole (14)**: 3-Prenylindole[x] (200 mg, 1.08 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 and stirred at RT. NBu_4Cl (30 mg, 0.11 mmol, 10 mol%), powdered NaOH (86 mg, 2.16 mmol, 2.0 equiv.) and tosyl chloride (226 mg, 1.19 mmol, 1.2 equiv.) were added subsequently and the resulting mixture was stirred at RT for 1 h. Hydrochloric acid (2 mL, 1 M) and water (10 mL) were added, the phases were separated and the aqueous phase was extracted with CH_2Cl_2. The organic phases were combined, dried over sodium sulfate and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (pentane:Et_2O:CH_2Cl_2 = 80:15:5) to give **15** as a coluorless oil (319 mg, 0.94 mmol, 87%) **IR (film)**: 2977, 2922, 1597, 1447, 1367, 1187, 1121, 1095, 974, 744, 669. **^{1}H-NMR** (400 MHz, $CDCl_3$, 295 K) δ = 8.02-7.96 (m, 1H), 7.78-7.72 (m, 2H), 7.49-7.45 (m, 1H), 7.34-7.28 (m, 2H), 7.27-7.18 (m, 3H), 5.41-5.34 (m, 1H), 3.38-3.32 (m, 2H), 2.33 (s, 3H), 1.78 (s, 3H), 1.73 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$, 295 K): δ = 144.8, 135.6, 135.5, 133.8, 131.1, 129.9, 126.9, 124.7, 123.1, 122.9, 122.8, 120.9, 119.7, 113.8 25.8, 24.0, 21.7, 18.0. **MS-ESI-EM**: calculated for $C_{20}H_{21}NNaO_2S^+$: 362.1185 ([M+Na$^+$]), found: 362.1193.

Preparation of 2-BArF: In a Schlenk-flask **2-Br$_3$** (0.86 g, 1.46 mmol, 1.0 equiv.)[5] and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (1.30 g 1.46 mmol, 1.0 equiv.) were dissolved in CH_2Cl_2 (50 mL) and stirred at RT overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The crude product was crystallized from CH_2Cl_2 (50 mL) and hexane (50 mL) at -20 °C overnight. The precipitate was filtered of and dried *in vacuo* to give the desired product as a pale yellow solid (1.40 g, 11.6 mmol, 79%). **MP:** 129-131 °C. **IR** (solid): 2940, 2869, 2362, 1610, 1457, 1355, 1278, 1126, 889, 839, 712, 682. **^{1}H-NMR** (600 MHz, CD_2Cl_2, 299 K): δ = 7.76-7.72 (m, 8H), 7.58 (s, 4H), 3.07 (s, 4H), 2.59-2.50 (m, 8H), 2.29-2.17 (m, 12H), 2.04 (s, 4H). **^{13}C-NMR** (126 MHz, CD_2Cl_2, 193 K): δ = 161.5 (q, $^1J_{C\text{-}B}$ = 49 Hz), 157.0 (s), 134.3 (s), 128.3 (qm, $^2J_{C\text{-}F}$ = 32 Hz), 122.0 (q, $^1J_{C\text{-}F}$ = 273 Hz), 117.3 (m), 41.4, 36.8, 35.8, 26.3. **^{11}B-NMR** (160 MHz, CD_2Cl_2, 193 K): δ = -6.8. **^{19}F-NMR** (470 MHz, CD_2Cl_2, 193 K): δ = -62.4. **MS-ESI-EM**: *m/z* = 347.1369 calculated for $C_{20}H_{28}Br^+$ ([M]$^+$), *found*: 347.1372; 863.1 calculated for $C_{32}H_{12}F_{24}B^-$ ([M]$^-$), *found*: 863.2. **Elementary analysis:** C: 51.55 H: 3.33 calculated for $C_{52}H_{40}BBrF_{24}$, *found*: C: 51.56 H: 3.41. For crystal structure analysis data of **2-BArF**, see supporting information and CCDC 1540672.

Preparation of 2-Al$_2$Br$_7$: In a Schlenk-flask $AlBr_3$ (750 mg, 2.81 mmol, 2.0 equiv.) and adamantylidene adamantane **1** (377 mg, 1.41 mmol, 1.0 equiv.) were dissolved in 1,2-dichlorobenzene (10 mL) at 0 °C. Br_2 (36 µL, 1.41 mmol, 1.0 equiv.) was added und the reaction mixture was allowed to reach RT. Dry pentane (20 mL) was added to crystallize the

product overnight at -20 °C. The supernatant solvent was removed and the precipitate was washed with dry pentane to give the desired product as a yellow solid (890 mg, 0.93 mmol, 66 %). **MP:** 115-117 °C. **^{1}H-NMR** (400 MHz, CD_2Cl_2, 299 K): δ = 3.13 (s, 4H, H-2), 2.69-2.58 (m, 4H, H-3'a), 2.57-2.51 (m, 4H, H-3a), 2.34-2.20 (m, 12H, H-3b, H-3'b + H-4, H-4'), 2.07 (s, 4H, H-5). **^{13}C-NMR** (101 MHz, CD_2Cl_2, 299 K): δ = 159.8 (C-1), 44.0 (C-3'), 41.5 (C-3), 38.5 (C-2), 37.1 (C-5), 27.5 (C-4, C-4'). **MS-ESI-EM**: *m/z* = 347.1369 calculated for $C_{20}H_{28}Br^+$ ([M]$^+$), *found*: 347.1370. For crystal structure analysis data of **2-Al$_2$Br$_7$**, see supporting information and CCDC 1540669.

Bromination of phosphines with 2-BArF

The suitability of **2-BArF** for the bromination of phosphines was investigated by NMR experiments according to the following general procedure: The phosphine (0.1 mmol) was added to a stirred solution of 2-BArF (0.1 mmol) in CD_2Cl_2 (1 mL). After stirring the solution for 5 minutes at room temperature, NMR analysis was performed. In all cases, the reaction mixture showed the clean formation of the bromophosphonium salt. No decomposition of the product was observed upon heating the NMR tube at 80 °C overnight.

Compound **4a**: **^{1}H-NMR** (400 MHz, CD_2Cl_2, 300 K): δ = 7.94-7.88 (m, 3H, aryl-H), 7.78-7.71 (m, 6H, aryl-H and 8H, BArF-H), 7.70-7.62 (m, 3H, aryl-H), 7.55 (s, 4H, BArF-H). **^{13}C-NMR** (101 MHz, CD_2Cl_2, 300 K): δ = 162.4 (q, $^1J_{C\text{-}B}$ = 50 Hz, BArF-C1), 137.9 (d, $J_{C\text{-}P}$ = 3 Hz, aryl-C), 135.4 (s, BArF-C2,C6), 134.3 (d, $J_{C\text{-}P}$ = 13 Hz, aryl-C), 131.4 (d, $J_{C\text{-}P}$ = 15 Hz, aryl-C), 129.5 (m, BArF-C3,C5), 125.1 (q, $^1J_{C\text{-}F}$ = 274 Hz, BArF-CF_3), 119.5 (d, $J_{C\text{-}P}$ = 88 Hz, aryl-C), 118.1 (m, BArF-C4). **^{31}P-NMR** (162 MHz, CD_2Cl_2, 300 K): δ = 52.9 (s). **MS-ESI-EM**: *m/z* = 342.0168 calculated for $C_{18}H_{16}BrP^+$ ([M]$^+$), found: 342.0167.

Compound **4b**: **^{1}H-NMR** (400 MHz, CD_2Cl_2, 300 K): δ = 7.83-7.77 (m, 3H, aryl-H), 7.76-7.71 (m, 8H, BArF), 7.63-7.57 (m, 3H, aryl-H), 7.56 (s, 4H, BArF), 7.52-7.45 (m, 3H, aryl-H), 7.42-7.32 (m, 3H, aryl-H), 2.40 (s, 3H, CH_3). **^{13}C-NMR** (101 MHz, CD_2Cl_2, 300 K): δ = 162.4 (q, $^1J_{C\text{-}B}$ = 50 Hz, BArF-C1), 145.1 (d, $J_{C\text{-}P}$ = 10 Hz, aryl-C), 137.9 (d, $J_{C\text{-}P}$ = 3 Hz, aryl-C), 135.7 (d, $J_{C\text{-}P}$ = 16 Hz, aryl-C), 135.4 (s, BArF-C2,C6), 135.3 (d, $J_{C\text{-}P}$ = 13 Hz, aryl-C), 129.5 (qm, $^2J_{C\text{-}F}$ = 32 Hz, BArF-C3,C5), 128.7 (d, $J_{C\text{-}P}$ = 15 Hz, aryl-C), 125.2 (q, $^1J_{C\text{-}F}$ = 273 Hz, BArF-CF_3), 118.1 (m, BArF-C4), 116.8 (d, $J_{C\text{-}P}$ = 83 Hz, aryl-C), 23.2 (d, $^3J_{C\text{-}P}$ = 15 Hz, CH_3). **^{31}P-NMR** (162 MHz, CD_2Cl_2, 300 K): δ = 46.4 (s). **MS-ESI-EM**: *m/z* = 383.0559 calculated for $C_{21}H_{21}BrP^+$ ([M]$^+$), found: 383.0552.

Compound **4c**: **^{1}H-NMR** (400 MHz, CD_2Cl_2, 300 K): δ = 7.91-7.82 (m, 4H, Ph), 7.81-7.72 (m, 10H, Ph, BArF), 7.70-7.63 (m, 4H, Ph), 7.62-7.59 (m, 2H, aryl-H), 7.56 (s, 4H, BArF), 7.43-7.36 (m, 2H, aryl-H), 4.74 (sept, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, $CHMe_2$), 1.45 (d, $^3J_{H\text{-}H}$ = 7.0 Hz, 12H, CH_3). **^{13}C-NMR** (101 MHz, CD_2Cl_2, 300 K): δ = 162.4 (q, $^1J_{C\text{-}B}$ = 50 Hz, BArF-C1), 137.9 (d, $J_{C\text{-}P}$ = 3 Hz, Ph), 135.4 (s, BArF-C2,C6), 132.0 (d, $J_{C\text{-}P}$ = 13 Hz, Ph), 130.6 (d, $J_{C\text{-}P}$ = 15 Hz, Ph), 129.5 (m, BArF-C3,C5), 125.2 (q, $^1J_{C\text{-}F}$ = 273 Hz, BArF-CF_3), 125.1 (s, aryl-C), 118.1 (m, BArF-C4), 113.9 (s, aryl-C), 50.2 ($CHMe_2$), 20.8 (CH_3). **^{31}P-NMR** (162 MHz, CD_2Cl_2, 300 K): δ = 16.8 (s). **MS-ESI-EM**: *m/z* = 480.1204 calculated for $C_{25}H_{28}N_3BrP^+$ ([M]$^+$), found: 480.1201.

Bromination of diethyl sulfide with 2-BArF

The suitability of **2-BArF** for the bromination of diethyl sulfide (**5**) was investigated by NMR experiments according to the following general procedure: **2-BArF** (36 mg, 0.03 mmol) was dissolved in CD_2Cl_2 (1 mL). This was followed by the addition of diethyl sulfide (**5**) in different quantities: sample A (Figure 3): no addition; sample C (Figure 3): 3.2 µL (0.03 mmol, 1.0 equiv.); sample D (Figure 3): 16 µL (0.15 mmol, 5.0 equiv.). The solutions were mixed by shaking and submitted to NMR measurements. Corresponding experiments were also carried out with tetrahydrothiophene, thioanisole and dibutylselenide[x] in place of diethylsulfide (see supporting information for details and NMR spectra).

Preparation of 7: **2-BArF** (125 mg, 0.1 mmol) was placed in a 2 mL glass vial and dissolved in CH_2Cl_2 (1 mL). Diethyl sulfide (**5**) (0.1 mL, 1.0 mmol, 10.0 equiv.) was added, the solution was briefly shaken and the glass vial was placed in a 10 mL glass vial. The area between the larger and the smaller vial was filled with pentane (ca. 2 mL) and the larger vial was closed with a screw cap and left standing at RT. After large crystals had appeared the larger vial was opened, the small vial was removed and the remaining solvent in the small vial was removed via a pipette. The colourless, crystalline solid from the small vial was dried *in vacuo* to give **7** (75 mg, 0.63 mmol, 61%). **^{1}H-NMR** (600 MHz, CD_2Cl_2, 299 K): δ = 7.74-7.71 (m, 8H), 7.56 (s, 4H), 2.58 (q, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H), 2.35-2.05 (m, 22H), 1.97-1.88 (m, 4H), 1.69-164 (m, 1H), 1.61 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 3H). **^{13}C-NMR** (151 MHz, CD_2Cl_2, 299 K): δ = 162.3 (q, $^1J_{C\text{-}B}$ = 50 Hz), 135.3, 129.4 (qm, $^2J_{C\text{-}F}$ = 32 Hz), 125.2 (q, $^1J_{C\text{-}F}$ = 273 Hz), 118.0 (m), 97.1, 39.4, 38.9, 38.7, 37.6, 36.5, 34.5, 31.1, 27.0, 27.0, 24.7, 13.1. **^{11}B-NMR** (160 MHz, CD_2Cl_2, 299 K): δ = -6.6. **^{19}F-NMR** (564 MHz, CD_2Cl_2, 299 K): δ = -62.9. **MS-ESI-EM**: *m/z* = 329.2298 calculated for $C_{22}H_{33}S^+$ ([M]$^+$), *found*: 329.2313. For crystal structure analysis data of **7**, see supporting information and CCDC 1540673.

General procedure for bromocylization of poylenes: In a Schlenk-flask starting material **8** (0.40 mmol, 1.00 equiv.) and HMDS (129 mg, 0.8 mmol 2.00 equiv.) were dissolved in CH_2Cl_2 (3 mL) and cooled to 0 °C. **2-BArF** (0.20 mmol, 242 mg, 1.00 equiv.) was added and the resulting solution stirred for 3 h. After addition of $NaHCO_3$ (*aq.*, 10%, 2.5 mL) and Na_2SO_4 (*aq.*, 10%, 2.5 mL) the aqueous phase was extracted with CH_2Cl_2 (3x5 mL) the combined organic phases were dried over $MgSO_4$ and the solvent removed *in vacuo*. Purification by column chromatography provided the product **9**.

***rac*-(2*S**,4a*S**,10a*R**)-2-Bromo-1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-trimethyl-phenantrene (9a):** Following the general procedure **8a** (91 mg, 0.40 mmol, 1.0 equiv.) was cyclized. Purification by column chromatography (pentane) provided **9a** as a colourless liquid (79 mg, 0.26 mmol, 64%) containing about 10% impurities. Crystallization from acetone provided **9a** as a colourless crystalline solid (32 mg, 0.10 mmol, 26%). **MP.**: 97 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K): δ = 7.23-7.19 (m, 1H), 7.17-7.04 (m, 3H), 4.11-4.02 (m, 1H), 3.02-2.83 (m, 2H), 2.44-2.22 (m, 3H), 2.03-1.95 (m, 1H), 1.90-1.76 (m, 1H), 1.66-1.55 (m, 1H), 1.53-1.45 (m, 1H), 1.26 (s, 3H), 1.17 (s, 3H), 1.08 (s, 3H), **^{13}C-NMR** (101 MHz, $CDCl_3$, 299 K): δ = 148.8, 134.8, 129.2, 126.0, 125.7, 124.6, 69.0, 51.3, 40.2, 40.0, 38.0, 31.7, 30.9, 30.7, 25.0, 20.7, 18.4, **MS-ESI-EM** (with added AgOTFA): *m/z* = 413.0029 calculated for $C_{17}H_{23}BrAg^+$ ([M+Ag]$^+$), found: 413.0029. For crystal structure analysis data of **5a**, see supporting information and CCDC 1540671.

***rac*-(2*S**,4a*S**,10a*R**)-2-Bromo-1,2,3,4,4a,9,10,10a-octahydro-6-*iso*-propyl-1,1,4a-trimethylphenantrene (9b):** Following the general procedure **8b** (108 mg, 0.4 mmol, 1.0 equiv.) was cyclized. Purification by column chromatography (pentane) provided **9b** as a colourless solid (39 mg, 0.11 mmol, 29%). **MP.**: 112-113 °C, **IR** (film): 2958, 2871, 1499, 1461, 1392, 1378, 1264, 1184, 909, 733, 646, 540, 535, 530, 525, 519, **^{1}H-NMR** (400 MHz, $CDCl_3$, 295 K): δ = 7.05 (s, 1H), 7.02-6.98 (m, 2H), 4.05 (dd, $^3J_{H\text{-}H}$ = 12.4, 4.4 Hz, 1H), 2.92-2.79 (m, 3H), 2.43-2.23 (m, 3H), 1.99-1.91 (m, 1H), 1.86-1.75 (m, 1H), 1.67-1.58 (m, 1H), 1.47 (dd, $^3J_{H\text{-}H}$ = 12.0, 2.1 Hz, 1H), 1.25 (d, $^4J_{H\text{-}H}$ = 0.5 Hz, 3H), 1.22 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H), 1.15 (s, 3H), 1.06 (s, 3H), **^{13}C-NMR** (75 MHz, $CDCl_3$, 295 K): δ = 148.7, 146.5, 132.3, 129.1, 123.8, 122.7, 69.2, 51.5, 40.2, 40.0, 38.1, 34.2, 31.7, 30.7, 30.6, 25.1, 24.3, 24.3, 20.8, 18.4. **MS-ESI-EM** (with added AgOTFA): m/z = 455.0498 calculated for $C_{20}H_{29}BrAg$ ([M+Ag]$^+$), found: 455.0498. For crystal structure analysis data of **5b**, see supporting information and CCDC 1540670.

***rac*-(2*S**,4a*S**,10a*R**)-2-Bromo-1,2,3,4,4a,9,10,10a-octahydro-6-methoxy-1,1,4a-trimethyl-phenantrene (9c):** Following the general procedure **8c** (103 mg, 0.4 mmol, 1.0 equiv.) was cyclized. Purification by column chromatography (pentane) provided **9c** as a colourless liquid (67 mg, 0.20 mmol, 50%) containing about 10% impurities. Crystallization from acetone provided **9c** a colourless crystalline solid (41 mg, 0.12 mmol, 30%). **MP.**: 110-111 °C, **^{1}H-NMR** (300 MHz, $CDCl_3$, 299 K): δ = 6.98 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 1H), 6.75 (d, $^3J_{H\text{-}H}$ = 2.6 Hz, 1H), 6.68 (dd, $^3J_{H\text{-}H}$ = 8.4, 2.6 Hz, 1H), 4.05 (dd, $^3J_{H\text{-}H}$ = 12.5, 4.1 Hz), 3.77 (s, 3H), 2.96-2.74 (m, 2H), 2.39-2.22 (m, 3H), 2.01-1.90 (m,1H), 1.86-1.75 (m, 1H), 1.66-1.58 (m, 1H), 1.45 (dd, $^3J_{H\text{-}H}$ = 12.0,2.1 Hz, 1H), 1.25 (d, $^4J_{H\text{-}H}$ = 0.5 Hz, 3H), 1.16 (s, 3H), 1.06 (s, 3H).**^{13}C-NMR** (75 MHz, $CDCl_3$, 299 K): δ = 157.9, 150.1, 130.0, 127.1, 111.2, 110.3, 69.0, 55.4, 51.4, 40.2, 40.0, 38.2, 31.7, 30.7, 30.1, 24.9, 20.9, 18.4. **MS-ESI-EM** (with added AgOTFA): *m/z* = 445.0123, calculated for $C_{18}H_{25}BrOAg^+$ ([M+Ag]$^+$), found: 445.0122.

***rac*-2-bromo-6-methoxy-1,1-dimethyl-1,2,3,4-tetrahydronaphthaline (12):** According to the general procedure **11** (38 mg, 0.20 mmol, 1.0 equiv.) was cyclized. Purification by column chromatography (pentane) provided **12** as a colourless solid (18 mg, 0.07 mmol, 34%). **IR** (film): 2973, 2947, 2836, 2364, 2337, 1578, 1469, 1451, 1438, 1261, 1081, 780, 740, 566, 558, 546, 531, 513. **^{1}H-NMR** (400 MHz, $CDCl_3$, 296 K): δ = 7.06-7.00 (m, 1H), 6.68-6.64 (m, 1H), 6.64-6.60 (m, 1H), 4.33 (dd, $^3J_{H\text{-}H}$ = 9.3, 3.1 Hz, 1H), 3.74 (s, 3H), 3.04-2.90 (m, 1H), 2.89-2.74 (m, 1H), 2.35-2.13 (m, 2H), 1.48 (s, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$, 296 K): δ = 158.9, 136.4, 131.3, 126.9, 121.8, 109.5, 68.5, 55.2, 39.4, 30.5, 30.1, 27.4, 25.8. **MS-ESI-EM** (with added AgOTFA): *m/z* = 642.9978 calculated for $(C_{13}H_{17}BrO)_2Ag^+$ ([2M+Ag]$^+$), found: 642.9975.

***rac*-2-bromo-3,3-dimethyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[b]-indole (15)**: According to the general procedure *N*-Ts-3-prenylindole **14** (140 mg, 0.40 mmol, 1.0 equiv.) was cyclized. Purification by column chromatography (pentane/CH_2Cl_2: 1/1) provided **15** as a colourless oil (55 mg, 0.13 mmol, 33%). **IR (film)**: 2966, 2933, 1597, 1363, 1174, 1132, 991, 807, 745, 666, 571. **^{1}H-NMR** (500 MHz, $CDCl_3$, 299 K): δ = 8.12-8.09 (m, 1H), 7.68-7.64 (m, 2H), 7.38-7.35 (m, 1H), 7.31-7.23 (m, 2H), 7.22-7.19 (m, 2H), 4.48 (dd, $^3J_{H\text{-}H}$ = 9.4, 7.5 Hz, 1H), 3.30 (dd, $^2J_{H\text{-}H}$ = 14.8, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H), 3.00 (dd, $^2J_{H\text{-}H}$ = 14.8, $^3J_{H\text{-}H}$ = 9.4 Hz, 1H), 2.35 (s, 3H), 1.56 (s, 3H), 1.48 (s, 3H). **^{13}C-NMR** (126 MHz, $CDCl_3$, 299 K): δ = 148.8, 144.8, 140.2, 136.5, 129.9, 126.5, 125.9, 124.5, 123.8, 119.4, 115.3, 62.5, 47.0, 33.5, 25.4, 23.4, 21.7. **MS-ESI-EM**: m/z = 440.0290 calculated for $C_{20}H_{20}NNaO_2S$ ([M+Na]$^+$), found: 440.0289.

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Keywords: alkenes • cations • cyclization • electrophilic addition • halogenation

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Unidentified ethyl group: ^{1}H-NMR (400 MHz, CD_2Cl_2): 3.07 (q, *J* = 7.1 Hz), 1.41 (t, *J* = 7.1 Hz); ^{13}C-NMR (101 MHz, CD_2Cl_2): 34.5, 15.5.

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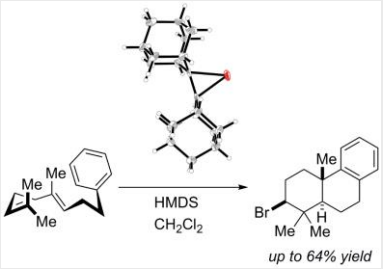
Sterically demanding bromiranium ions with weakly coordinating counterions are highly reactive electrophilic brominating agents. Despite their high reactivity these reagents are stable and can be applied in electrophilic halogenations of alkenes as well as heteroatoms.



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Stable Bromiranium Ions with Weakly-Coordinating Counterions as Efficient Electrophilic Brominating Agents