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Halogen and Chalcogen Cation Pools Stabilized by DMSO. Versatile Reagents for Alkene Difunctionalization

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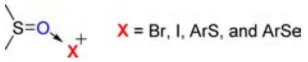
Supporting Information

ABSTRACT: Halogen and chalcogen cations ($X^+ = Br^+$, I^+, ArS^+, and $ArSe^+$) were generated by low-temperature electrochemical oxidation in the presence of dimethyl sulfoxide (DMSO) and were accumulated in the solution. DFT calculations indicated that DMSO stabilizes these cations by coordination. The complexes of I^+ with one and two DMSO molecules were observed by cold-spray-ionization MS analyses. The stability of the resulting cation pools of X^+ increased in the order of $Br^+ < I^+ < ArS^+ < ArSe^+$, which could be explained in terms of the electronegativity of X. The cation pools served as versatile reagents for organic synthesis; the reactions with alkenes gave *β*-X-substituted alkoxysulfonium ions, which were converted to the corresponding carbonyl compounds by the treatment with triethylamine, whereas the treatment with methanol gave the corresponding alcohols. The reactions with aminoalkenes and 1,6-dienes gave the cyclized products.

Scheme 1. Halogen and Chalcogen Cations Stabilized by DMSO



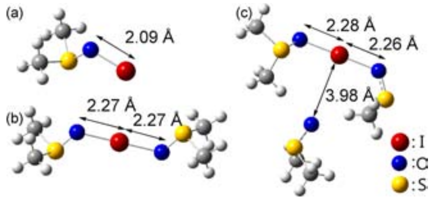


Figure 1. Structures of (a) DMSO−I^+, (b) $(DMSO)_2$−I^+, and (c) $(DMSO)_3$−I^+ indicated by DFT calculation on the level of B3LYP/6-31G(d) and LANL2DZ (with ECP) for I.

Organic molecules bearing halogens and chalcogens not only serve as powerful intermediates in organic syntheses but also functional materials and biologically active compounds.[1] Although a wide variety of methods for introducing such elements into organic molecules have been developed so far, one of the most straightforward and powerful methods would be the use of highly reactive halogen cations and monovalent chalcogen cations.[2] However, such species are usually too unstable to accumulate in the solution, and therefore they are difficult to use as reagents.

The electrochemical oxidation[3,4] provides a powerful method for generating and accumulating highly reactive cationic species in the solution (the "cation pool" method),[3c,5] whereas the chemical methods are not effective because of reversibility of cation generation.[6,7] Although some carbocations and onium ions[8] can be accumulated as cation pools at low temperatures, halogen and chalcogen cations are difficult to accumulate in the solution as "cation pools" because they are too unstable.

One potential method to solve this problem would be the use of a stabilizing agent that coordinates the cation being generated. The crucial point for the success of this approach is choosing an appropriate stabilizing agent. To date, only a few stabilizing agents have been reported. For example, Miller and co-workers reported the generation and accumulation of "I^+" cation in acetonitrile (CH_3CN),[9,10] and later we reported the detection of CH_3CN−I^+ and $(CH_3CN)_2I^+$ by cold-spray-ionization mass spectroscopy.[11] Shono and co-workers reported that "I^+" could be accumulated in trimethyl orthoformate (TMOF), and its reactivity was different from one generated in CH_3CN.[12] Moreover, we reported that arylsulfenium ions (ArS^+) could be accumulated in the presence of diaryl disulfide (ArSSAr).[13] We have been searching for a more versatile stabilizing agent for a wide variety of reactive cations, and herein we report that dimethyl sulfoxide (DMSO) can be generally used as a stabilizing agent for halogen and chalcogen cations (Scheme 1) and that the pools of the stabilized cations serve as powerful reagents for alkene difunctionalization. Also, the use of DMSO leads to a useful synthetic transformation, because the alkoxysulfonium ion intermediates can be converted to carbonyl compounds via Swern−Moffatt type oxidation[14,15] by taking advantage of reaction integration using reactive intermediates.[16,17]

We began by studying the nature of I^+/DMSO[18] by computational calculations (Figure 1).[19,20] For comparison, I^+/CH_3CN and I^+/TMOF systems were also studied. The DFT calculations indicated that I^+ forms a complex with DMSO in the gas phase. The oxygen atom of DMSO interacts with I^+ (I−O distance: 2.09 Å), and the stabilization energy is 118.9 kcal/mol. The coordination by the second DMSO also causes further stabilization (36.1 kcal/mol). The interaction with the third DMSO somewhat stabilizes I^+ (7.5 kcal/mol), but the I−O distance is much longer (3.98 Å), indicating the third DMSO does not directly coordinate to I^+. In the case of CH_3CN, the calculations indicated that I^+ forms a complex with CH_3CN in

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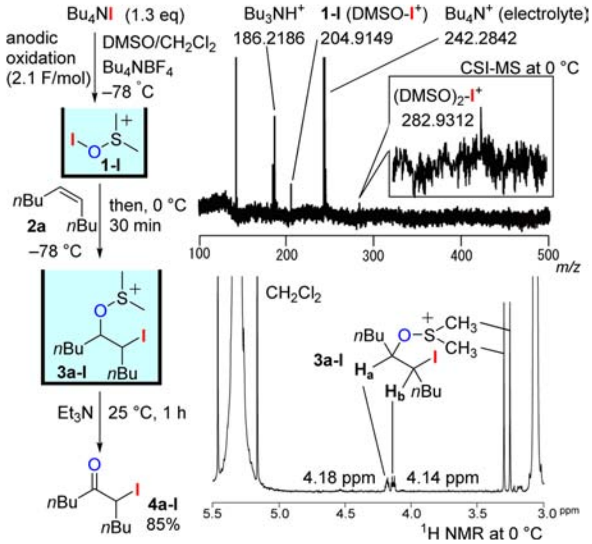


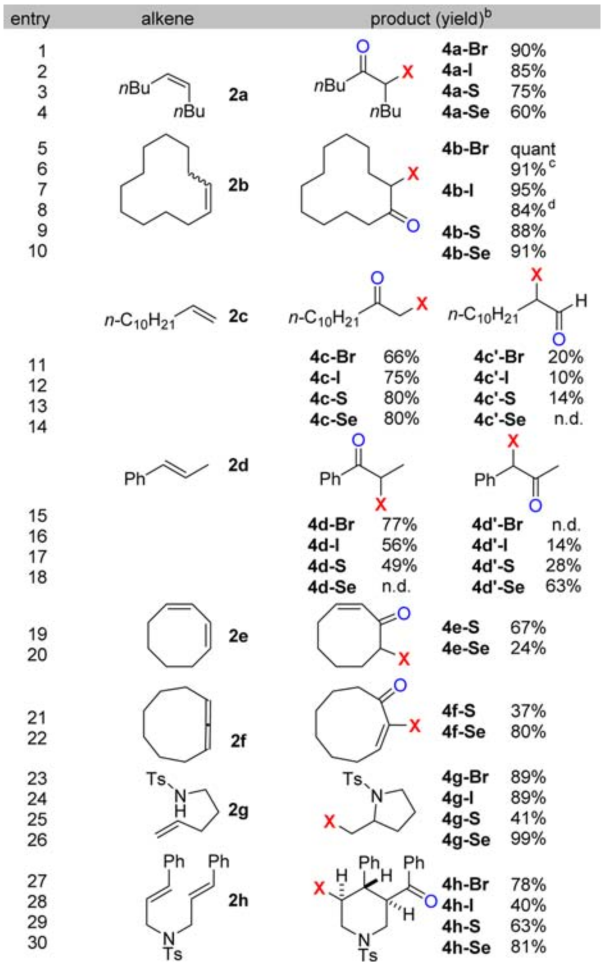
Figure 2. Generation of I^+/DMSO **1-I**, and its reaction with an alkene. CSI-MS and ^1H NMR analyses.

gas phase, but stabilization energy (101.5 kcal/mol) is smaller than that for DMSO. The further stabilization energy by the second CH_3CN (31.6 kcal/mol) is also smaller than that for DMSO. It is interesting that I^+ does not form a stable complex with a single TMOF molecule in gas phase whereas it forms a stable complex with two molecules of TMOF. However, total stabilization energy with two TMOF (130 kcal/mol) is smaller than those for two DMSO and two CH_3CN. Therefore, the computational studies indicated that stabilizing ability of DMSO to I^+ is stronger than those of CH_3CN and TMOF.

With the information obtained by the computational studies in hand, we next performed the experimental studies on the generation of I^+/DMSO (**1-I**) cation pool. The electrochemical oxidation of Bu_4NI was carried out in a divided cell in DMSO/CH_2Cl_2 (1:9 v/v) using Bu_4NBF_4 as a supporting electrolyte at −78 °C. After 2.1 F/mol of electricity was consumed, the resulting solution was analyzed by the cold-spray-ionization mass spectroscopy (CSI-MS)[21] at 0 °C, which showed the peaks due to DMSO−I^+ and $(DMSO)_2$−I^+ species (Figure 2, top). (*Z*)-5-Decene (**2a**) was added to the solution, and the mixture was stirred at 0 °C. Although **1-I** could not be characterized by NMR, the resulting *β*-iodo alkoxysulfonium ion **3a-I** could be well characterized by NMR (Figure 2, bottom). The cross peak of the HMQC spectrum indicated that a signal at 4.18 ppm (^1H NMR) is due to the proton (H_a) attached to the carbon ($\delta = 91.4$ ppm in ^{13}C NMR) adjacent to the oxygen atom derived from DMSO. A signal at 4.14 ppm could be assigned to the proton attached to the carbon adjacent to the iodine atom. The HMQC spectrum also indicated that two singlet signals at 3.26 and 3.30 ppm (^1H NMR) are due to the protons attached to the methyl carbons derived from DMSO. The formation of **3a-I** indicated that **1-I** having the interelement bond[22] served as both a nucleophile and an electrophile toward the carbon−carbon double bond. Treatment of **3a-I** with triethylamine gave *α*-iodo ketone **4a-I**. It is also noteworthy that the electrochemical oxidation of Bu_4NI in the absence of DMSO at −78 °C followed by the addition of **2a** and DMSO and subsequent treatment with triethylamine did not give **4a-I**, indicating that I^+ could not be accumulated in the solution in the absence of DMSO.

As shown in Table 1, **1-I** reacted with various alkenes to give the corresponding *α*-iodo ketones. It is noteworthy that the electrochemical oxidation of I_2 instead of Bu_4NI was also effective for generating **1-I** (entry 8).

Table 1. Reactions of Alkenes with Halogen and Chalcogen Cation Pools Stabilized by DMSO (X^+/DMSO)[a]



entry	alkene	product	(yield)[b]	product	(yield)[b]
1	2a	4a-Br	90%		
2		4a-I	85%		
3		4a-S	75%		
4		4a-Se	60%		
5	2b	4b-Br	quant		
6			91%[c]		
7		4b-I	95%		
8			84%[d]		
9		4b-S	88%		
10		4b-Se	91%		
11	2c	4c-Br	66%	4c'-Br	20%
12		4c-I	75%	4c'-I	10%
13		4c-S	80%	4c'-S	14%
14		4c-Se	80%	4c'-Se	n.d.
15	2d	4d-Br	77%	4d'-Br	n.d.
16		4d-I	56%	4d'-I	14%
17		4d-S	49%	4d'-S	28%
18		4d-Se	n.d.	4d'-Se	63%
19	2e	4e-S	67%		
20		4e-Se	24%		
21	2f	4f-S	37%		
22		4f-Se	80%		
23	2g	4g-Br	89%		
24		4g-I	89%		
25		4g-S	41%		
26		4g-Se	99%		
27	2h	4h-Br	78%		
28		4h-I	40%		
29		4h-S	63%		
30		4h-Se	81%		

[a] The electrolysis of Bu_4NI and Bu_4NBr was carried out using 1.3 equiv of Bu_4NX (based on the alkene which was added after electrolysis) with 2.1 F/mol of electricity based on Bu_4NX. The electrolysis of ArSSAr and ArSeSeAr was carried out using 0.65 equiv of ArXXAr (based on the alkene which was added after electrolysis) with 2.1 F/mol of electricity based on ArXXAr. [b] Isolated yield. [c] The electrolysis was carried out using 0.65 equiv of Br_2 (based on the alkene which was added after electrolysis) with 2.1 F/mol of electricity based on Br_2. [d] The electrolysis was carried out using 0.65 equiv of I_2 (based on the amount of the alkene which was added after electrolysis) with 2.1 F/mol of electricity based on I_2.

It is noteworthy that electrochemically generated I^+/CH_3CN and I^+/TMOF are not effective for the present transformation. For example, the reaction of I^+/CH_3CN with **2b** in DMSO/CH_2Cl_2 followed by the treatment with triethylamine gave **4b-I** only in a low yield (39%). The use of I^+/TMOF did not give **4b-I** at all. The reaction of **2b** with *N*-iodosuccinimide (NIS) in DMSO/CH_2Cl_2 followed by the treatment with triethylamine resulted in recovery of **2b**. I_2, NIS, and NBS with IBX are well-known systems for transforming alkenes to *α*-halocarbonyl compounds.[23] However, in addition to the advantage of providing mild, easily scalable reaction conditions, the present electrochemical approach seems to be particularly more attractive from safety and environmental standpoints, because the use of hazardous and explosive[24] IBX can be avoided.

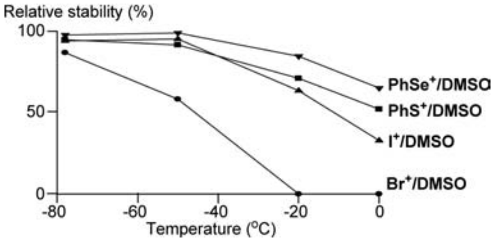


Figure 3. Thermal stability of DMSO−X^+ species.

We next examined the generation and reactions of Br^+/DMSO (**1-Br**). DFT calculations indicated that Br^+ is also stabilized by coordination of one or two DMSO molecules like **1-I**. The electrochemical oxidation of Bu_4NBr was carried out in the presence of DMSO at −78 °C. Although **1-Br** was not detected by NMR and CSI-MS analyses, the resulting solution reacted with **2a** to give β-bromo alkoxysulfonium ion **3a-Br**, which was characterized by ^1H and ^{13}C NMR. The subsequent treatment with triethylamine gave α-bromo ketone **4a-Br** (Table 1, entry 1). As shown in Table 1, **1-Br** also reacted with various alkenes to give the corresponding α-bromo ketones. Br_2 is also effective as a precursor of **1-Br** (entry 6).

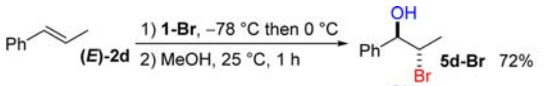
Next, we examined the generation and accumulation of chalcogenium ions stabilized by DMSO. DFT calculations indicated that the ArS and ArSe are also stabilized by coordination of one or two DMSO molecules. The electrochemical oxidation of bis(4-fluorophenyl) disulfide (ArSSAr, Ar = 4-FC_6H_4)[25] and that of diphenyl diselenide (ArSeSeAr, Ar = Ph)[26] at −78 °C followed by the addition of **2a** and subsequent treatment with triethylamine gave α-thio ketone **4a-S** (75%) and α-seleno ketone **4a-Se** (60%), respectively. The results indicated that ArS^+/DMSO[27] and $ArSe^+$/DMSO could be generated and accumulated in the solution as cation pools.

We next examined the relative stability of these species. Thus, the electrochemical oxidation reactions of Bu_4NBr, Bu_4NI, PhSSPh, and PhSeSePh were carried out at −78 °C, and the resulting solutions were warmed to a second temperature. After being kept there for 30 min, the solutions were cooled at −78 °C and were reacted with **2b**. After treatment with triethylamine, the yields of the corresponding ketones were determined. Relative stabilities were evaluated by the relative yields based on those not kept at the second temperature. As shown in Figure 3, Br^+ is the least stable. The stability increases in the order of $Br^+ < I^+ < PhS^+ < PhSe^+$. This tendency can be explained in terms of electronegativity of the cationic elements (Br: 2.96, I: 2.66, S: 2.58, and Se: 2.55).[28,29]

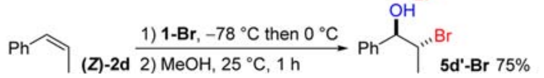
It is also interesting that the nature of the cationic elements also affected the regioselectivity of the addition to unsymmetrically substituted alkenes. The reaction of **1-Br** with terminal alkene **2c** gave ketone **4c-Br** as a major product and aldehyde **4c′-Br** as a minor product (entry 11). The amount of aldehyde decreased when **1-I** and **1-Se** were used (entries 12 and 13). The reaction of **1-Se** with **2c** gave ketone **4c-Se** exclusively. Aldehyde **4c′-Se** was not observed (entry 14). Low selectivity of **1-Br** might be explained in terms of higher reactivity of the three-membered ring bromonium ion intermediate than others, leading to less regioselective nucleophilic attack by DMSO.[30]

The regioselectivity for 1-phenyl-1-propene (**2d**) was more interesting. The reaction of **1-Br** with **2d** gave 2-bromo-1-phenylpropan-1-one (**4d-Br**) selectively (entry 15), whereas the reaction of **1-Se** with **2d** gave 1-phenyl-1-(phenylselanyl)propan-2-one (**4d′-Se**) selectively (entry 18). **1-I** and **1-S** gave mixtures of two products (entries 16 and 17). This remarkable contrast in regioselectivity might be explained in terms of the difference in electronegativity of X, although the detailed mechanism is not yet clear. The reaction of **1-Br** with **2d** would give the three-membered ring bromonium ion. However, a positive charge seems to be located mainly on the benzylic carbon rather than the electronegative Br. Therefore, DMSO attacks the benzylic carbon to give phenyl ketone **4d-Br** after treatment with triethylamine. The natural bond orbital (NBO) analysis[31] is consistent with this idea.[32] The charge on X of the three-membered ring onium ion intermediate decreases in the order of X = Se > S > I > Br, whereas the charge on the benzylic carbon increases in the order of X = Se < S < I < Br. The bond order between X and the benzylic carbon also decreases in the order of X = Se > S > I > Br.

Stereochemistry of the addition to C−C double bonds is another intriguing aspect of the chemistry of X^+/DMSO, although the stereochemistry is destroyed during Swern−Moffatt-type oxidation. To gain the information of the stereochemistry, an alkoxysulfonium ion intermediate was treated with methanol instead of triethylamine. Thus, both *E* and *Z* isomers of **2d** were reacted with **1-Br**, and the resulting solution was treated with methanol.[33] (***E***)-**2d** gave **5d-Br** (eq 1),



(1)



(2)

whereas (**Z**)-**2d** gave its diastereomer **5d′-Br** (eq 2), suggesting the addition of Br^+ and DMSO across the C−C double bond in an *anti* fashion, because it is known that methanol attacks the sulfur atom to cleave the O−S bond.[33] The *anti*-selectivity suggests a mechanism involving the back-side attack of DMSO in the bulk solution on the three-membered ring bromonium ion generated from Br^+ and an alkene.

1,3-Dienes reacted with **1-S** and **1-Se** to give α,β-unsaturated carbonyl compounds in moderate yields after treatment with triethylamine (entries 19 and 20), although the reactions with **1-Br** and **1-I** gave complex mixtures. The regiochemistry is interesting. DMSO attacked the inner carbon of the 1,3-diene selectively to give the 1,2-addition intermediate. The product derived from 1,4-addition was not obtained. Allenes also reacted with **1-S** and **1-Se** to give α,β-unsaturated carbonyl compounds (entries 21 and 22). In this case, DMSO attacked the terminal carbon of the allene selectively.

It is also interesting that halogen and chalcogen cation pools initiate alkene-cyclization reactions. Reactions of **1-X** with an alkene having a nucleophilic tosylamide group (**2g**) gave the cyclized pyrrolidine derivatives (entries 23−26), which are useful building blocks of biologically interesting compounds.[34]

The reaction of **1-X** with 1,6-diene **2h** is more interesting. The cyclized products **4h-X**, piperidine derivatives[34] having both the X substituent and a carbonyl group, were obtained as a single diastereomer after treatment with triethylamine (entries 27−30).

In conclusion, halogen cations (Br^+ and I^+) and monovalent chalcogen cations (ArS^+ and $ArSe^+$) stabilized by DMSO can be generated and accumulated as cation pools by low temperature electrochemical oxidations. The cations have both sufficient stability and marked reactivity toward alkenes. The reactions with alkenes gave the corresponding carbonyl compounds bearing a halogen or chalcogen substituent at the α-carbon after treatment with triethylamine. This new tactic will provide access to a wide range of chemical processes for making synthetic intermediates having halogen and chalcogen atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and spectroscopic data of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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