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PERSPECTIVE

Organic reactions mediated by electrochemically generated ArS^+

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Low-temperature electrochemical oxidation of ArSSAr was carried out to generate a pool of "ArS^+". Spectroscopic studies (^{1}H NMR and CSI-MS) of the resulting solution revealed the accumulation of $ArS(ArSSAr)^+$. The resulting "ArS^+" pool reacted with alkenes and alkynes to give diarylthio-substituted products. The "ArS^+" pool rapidly reacted with thioacetals to give the corresponding alkoxycarbenium ion pools, which reacted with various carbon nucleophiles (indirect cation pool method). The reaction of the alkoxycarbenium ion pools with stilbene derivatives in the presence of ArSSAr gave thiochroman derivatives. In addition to such stoichiometric reactions, a catalytic amount of "ArS^+" serves as an initiator and a chain carrier of some cationic chain reactions involving intramolecular carbon–carbon bond formation. *In situ* generation of "ArS^+" by electrochemical oxidation of ArSSAr with a catalytic amount of electricity in the presence of a substrate is also effective for such cationic chain reactions.

1 Introduction

Organic electrochemistry[1] provides a straightforward, efficient and tunable method for making and modifying organic molecules under mild conditions. The advantages of this method lie in its ability to oxidize or reduce organic compounds of a wide range of

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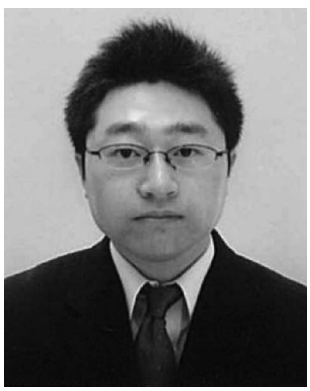


Kouichi Matsumoto

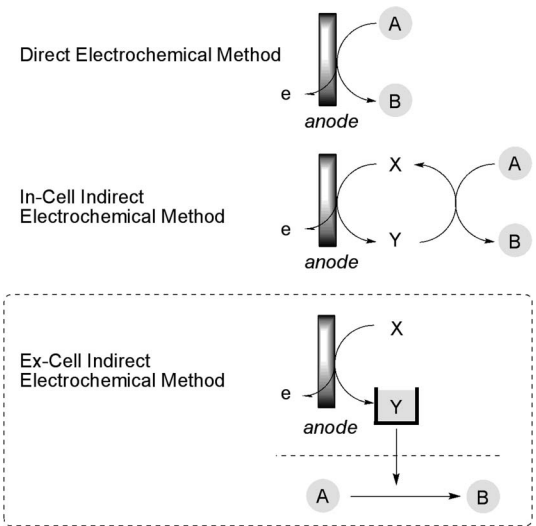
Kouichi Matsumoto was born in 1982 in Nara, Japan. He received his PhD from Kyoto University in 2010 under the supervision of Prof. Jun-ichi Yoshida. In 2010 he joined the group of Prof. Shigenori Kashimura at Kinki University as an Assistant Professor. His current research interests include electro-organic chemistry.

Seiji Suga

Seiji Suga was born in 1963 in Hiroshima. He received his PhD from Nagoya University under the supervision of Prof. Ryoji Noyori. He became a postdoctoral fellow (JSPS Postdoctoral Fellowships for Research Abroad) with Prof. Jack E. Baldwin at Oxford University. In 1996 he joined the group of Prof. Junichi Yoshida at Kyoto University as Instructor, and was promoted to Lecture (1999) and Associate Professor (2004). In 2008 he was appointed as Professor at Okayama University. His current research interests include electron-transfer reactions and synthetic processes of organic compounds.

oxidation and reduction potentials selectively generating highly reactive intermediates that are useful in organic synthesis.[2] It is also noteworthy that electrochemical processes are applicable to organic compounds bearing a variety of functional groups, because they usually proceed without using strong acids or bases. Based on such features, many synthetic transformations that are unique to electrochemistry have been developed so far. Thus, the electrochemical method opens new possibilities of synthesizing organic molecules of interesting functions and biological activities.

In general, the electrochemical methods are mainly classified into the following three types (Scheme 1):[3] the direct method, the in-cell indirect method and the ex-cell indirect method. In the direct electrochemical method, substrate **A** undergoes the electron transfer directly on the surface of the electrode to give product **B**. In the in-cell indirect electrochemical method, a mediator **X** undergoes the electron transfer on the surface of the electrode, and the resulting reactive species **Y** reacts with substrate **A** *in situ* to give product **B**, regenerating **X**. In the ex-cell indirect electrochemical method,[4] the direct electrochemical reaction of **X** is carried out to generate and accumulate reactive species **Y** in the first step. In the next step, **Y** is reacted with substrate **A** in the absence of electricity to give product **B**.



Scheme 1 Classification of electrochemical methods.

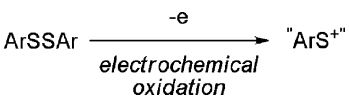
Jun-ichi Yoshida

Jun-ichi Yoshida was born in 1952. He graduated from Kyoto University in 1975, where he received his doctor's degree in 1981. In 1979 Yoshida joined the faculty at Kyoto Institute of Technology. In 1985 he moved to Osaka City University. In 1994 he was appointed as a full Professor of Kyoto University. Awards: the Progress Award of Synthetic Organic Chemistry, Japan (1987), the Chemical Society of Japan Award for Creative Work (2001), Nagoya Silver Medal (2006), Humboldt Research Award (2007), and Green and Sustainable Chemistry Award (2010). His research interests include integrated organic synthesis, organic electron transfer reactions, and microreactors.

We have developed the "cation pool" method in which highly reactive onium ions and carbocations are generated and accumulated by low-temperature electrochemical oxidation.[5] In the next step, the resulting reactive cations are reacted with carbon nucleophiles to obtain the corresponding carbon–carbon bond formation products. We also developed the "cation flow" method, in which reactive cations are generated and reacted with nucleophile in a flow system.[6] Recently, we have shown that a similar method can be applied to generation and reaction of highly reactive reagents[7] and catalysts. This approach widens the scope of the ex-cell indirect electrochemical method. In this perspective article, we overview our recent studies on a new ex-cell indirect electrochemical method using "ArS^+" [8] generated by low-temperature electrochemical oxidation of ArSSAr.

2 Generation of "ArS^+" by low-temperature electrochemical oxidation of ArSSAr and its characterization by spectroscopic studies

"ArS^+" is considered to be a highly electrophilic reagent,[9] although some doubts have been advanced of its existence in this form in the solution phase. Extensive studies on the chemical methods for generating "ArS^+" have been reported in the literature, which include chemical oxidation of ArSSAr[10] and the reactions of ArS–X with Lewis acids.[11] The electrochemical oxidation of ArSSAr serves as a useful method for generating "ArS^+" (Scheme 2). The radical cation of ArSSAr produced by one-electron oxidation of ArSSAr undergoes the cleavage of the sulfur–sulfur bond to give ArS^+ and $ArS^{\bullet}$. $ArS^{\bullet}$ is further oxidized to give ArS^+. Thus, the electrochemical generation, in principle, does not produce any by-products, and therefore is superior to the chemical generation, which uses toxic oxidizing reagents and produces byproducts derived from them.



Scheme 2 Electrochemical oxidation of ArSSAr.

The nature and the reactivity of electrochemically generated "ArS^+" depend on the electrolysis conditions (solvent, supporting electrolyte and temperature *etc.*). Simonet and co-workers assumed that ArS^+ is electrochemically generated as an intermediate in CH_2Cl_2, whereas they assumed that $ArSSAr^{2+}$ is generated in CH_3CN.[12] On the other hand, Tsuchida and co-workers reported the synthesis of oligo(*p*-phenylene sulfide (OPS) under acidic conditions. Presumably electrochemically generated ArS^+ reacted with ArSSAr *via* Friedel–Crafts type reactions.[13] In this case, $ArS(ArSSAr)^+$ [10] is suggested as an intermediate. Thus, there are several arguments on the chemistry of "ArS^+". Therefore, the characterization of electrochemically generated "ArS^+" has received significant research interest.

The electrochemical oxidation of ArSSAr (oxidation potential: 1.47 V (Ar = *p*-FC_6H_4)) is usually carried out in an H-type

cell equipped with a carbon felt anode and a platinum plate cathode (Fig. 1). In the anodic chamber is placed a solution of ArSSAr (0.4 mmol) in 0.3 M Bu_4NBF_4/CH_2Cl_2 (8 mL). In the cathodic chamber are placed 0.3 M Bu_4NBF_4/CH_2Cl_2 (8 mL) and trifluoromethanesulfonic acid (TfOH) (0.27 mmol) to facilitate the reduction of protons in the cathodic process. The constant current electrolysis (8 mA) is carried out at –78 °C with magnetic stirring.

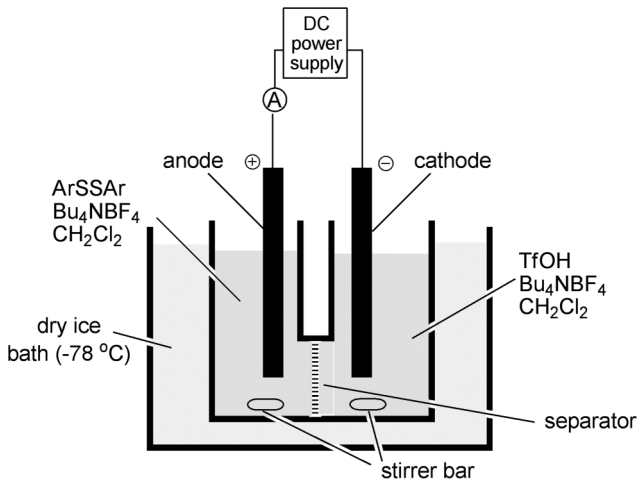


Fig. 1 An electrochemical apparatus consisting of an H-type divided cell and DC power supply for generation of "ArS$^+$" by the oxidation of ArSSAr at –78 °C.

The ^{1}H NMR (–80 °C) spectrum of the anodic solution obtained by the electrochemical oxidation of ArSSAr (Ar = *p*-FC_6H_4) in Bu_4NBF_4/CD_2Cl_2–CH_2Cl_2 [14] at –78 °C (0.67 F mol^{-1}) showed a spectrum similar to that of ArS(ArSSAr)$^+$ generated by the reaction of ArSSAr and $SbCl_5$.[10a,b] CSI-MS (cold-spray ionization mass spectroscopy)[15] (spray temperature: 0 °C) provided strong evidence for the formation of ArS(ArSSAr)$^+$ (m/z = 381) (Fig. 2). Therefore, it was concluded that ArS(ArSSAr)$^+$ was the species that was generated and accumulated by the low-temperature electrolysis of ArSSAr in Bu_4NBF_4/CH_2Cl_2.[16] In fact, 0.67 F mol^{-1} is the theoretical amount of electricity to convert ArSSAr to ArS(ArSSAr)$^+$.

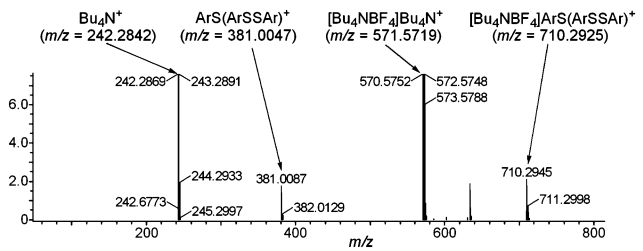
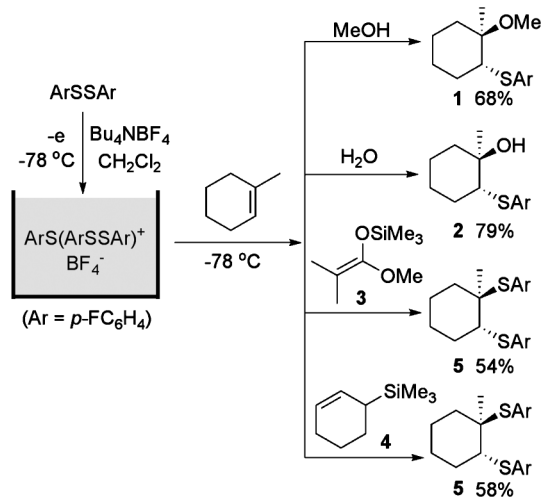


Fig. 2 CSI-MS analysis of electrochemically generated "ArS$^+$" (Ar = *p*-FC_6H_4) (spray temperature: 0 °C).

3 Stoichiometric reactions

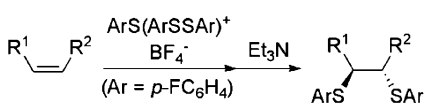
3.1 Reactions with alkenes and alkynes

The electrochemically generated ArS(ArSSAr)$^+BF_4^-$ rapidly reacts with an alkene even at low temperatures.[17] For example, the reaction of ArS(ArSSAr)$^+BF_4^-$ with 1-methylcyclohexene at –78 °C followed by quenching with MeOH as a nucleophile afforded adduct **1** (Markovnikov product) in 68% yield (Scheme 3). Presumably, the reaction proceeded by initial formation of an episulfonium ion intermediate.[18] A MeO group was introduced on the tertiary carbon, suggesting that MeOH attacked a partially developed carbocationic center. It is also noteworthy that the *anti* addition product was obtained exclusively. These observations are quite similar to those obtained for "ArS$^+$" generated by other methods in the absence of ArSSAr.[11] The use of H_2O as a quenching nucleophile led to the formation of **2** in a similar manner (Scheme 3).



Scheme 3 The reactions of ArS(ArSSAr)$^+BF_4^-$ (Ar = *p*-FC_6H_4) with 1-methylcyclohexene followed by addition of a quenching nucleophile.

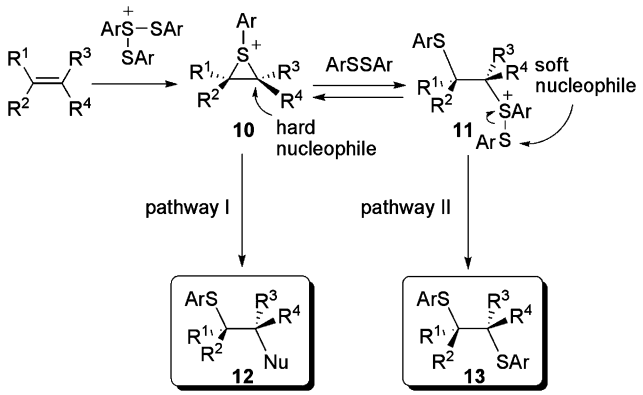
However, the use of ketene silyl acetal **3** as a quenching nucleophile led to *anti* addition of two ArS groups to give compound **5**. No appreciable carbon–carbon bond formation took place.[19] The formation of **5** indicated that ArSSAr attacked the episulfonium ion as a nucleophile. Use of an allylsilane, such as **4** as a quenching nucleophile also gave rise to the formation of **5**. Et_3N was also found to be an effective quenching nucleophile (Scheme 4). Diarylthio-substituted compounds were obtained in good yields (**6–9**). The stereoselectivity of the reactions was high, and *anti* addition products were obtained. Although several methods for this type of transformation have been reported in the literature,[20] the present method serves as an alternative convenient way to access such compounds.



R^1, R^2 = -$(CH_2)_4$-	**6** 72%
R^1 = C_6H_{13}, R^2 = H	**7** 66%
R^1 = R^2 = Ph	**8** 84%
R^1 = Ph, R^2 = CH_3	**9** 73%

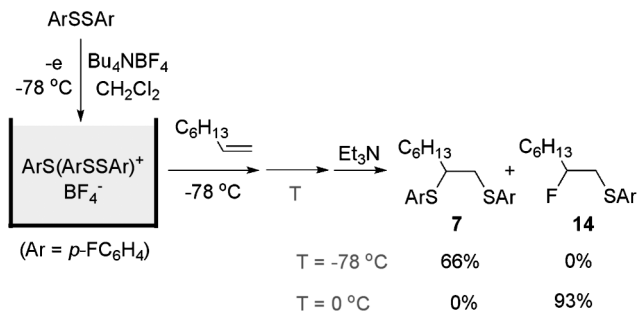
Scheme 4 The reactions of ArS(ArSSAr)$^+BF_4^-$ (Ar = *p*-FC_6H_4) with alkenes at –78 °C using Et_3N as a quenching nucleophile.

Although the reaction mechanism has not yet been fully clarified, the following mechanistic arguments seem to be reasonable (Scheme 5). In the first step, episulfonium ion intermediate[18] **10** is generated by the reaction of $ArS(ArSSAr)^+$ with an alkene. Nucleophilic attack of ArSSAr on **10** opens the three-membered ring to give sulfonium ion intermediate **11**. There is an equilibrium between **10** and **11**. A hard quenching nucleophile such as MeOH or H_2O selectively attacks **10** to give the corresponding product **12** (pathway I). On the other hand, a soft quenching nucleophile such as ketene silyl acetal **3**, allylsilane **4** and Et_3N selectively attacks **11** to cleave th alkoxycarbenium ion poolse S–S bond giving diarylthio-substituted compound **13** as the final product (pathway II).



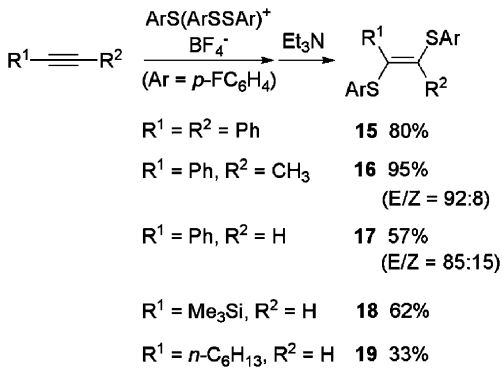
Scheme 5 Plausible reaction mechanism (Nu = nucleophile).

It is interesting that the reactions of $ArS(ArSSAr)^+BF_4^-$ with alkenes at higher temperatures give thiofluorinated product exclusively.[21,22] For example, thiofluorinated compound **14** was obtained exclusively in the reaction with 1-octene at 0 °C, whereas the reaction at −78 °C gave diarylthio-substituted compound **7** as shown in Scheme 6.[23] In this case, a fluoride ion, which is derived from the anionic part of supporting electrolyte (BF_4^-), attacked the episulfonium ion intermediate **10** as a nucleophile before a quenching reagent was added to the reaction mixture (Scheme 5).



Scheme 6 The reaction of $ArS(ArSSAr)^+BF_4^-$ (Ar = p-FC_6H_4) with 1-octene. The effect of reaction temperature.

The reactions of $ArS(ArSSAr)^+BF_4^-$ (Ar = p-FC_6H_4) with alkynes gave the corresponding diarylthio-substituted compounds (**15–19**), when a soft nucleophile such as Et_3N was used as a quenching nucleophile at −78 °C (Scheme 7).[17] The reactions are usually highly stereoselective, and *E*-isomers were obtained in high selectivity.



Scheme 7 Reactions of $ArS(ArSSAr)^+BF_4^-$ (Ar = p-FC_6H_4) with alkynes using Et_3N as a quenching reagent.

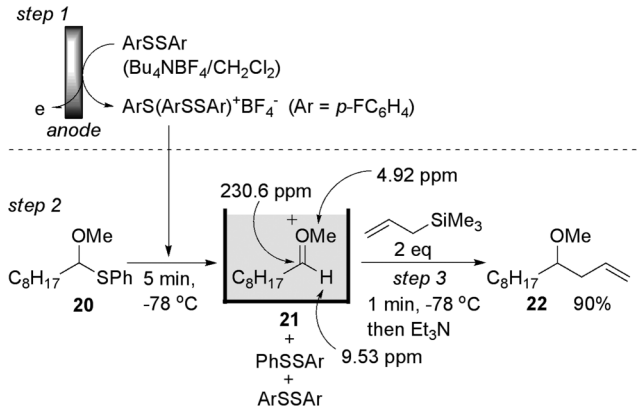
3.2 Reactions with thioacetals followed by reactions with carbon nucleophiles (indirect cation pool method)

In the "cation pool" method, carbocations stabilized by a neighboring heteroatom such as nitrogen (*N*-acyliminium ions),[24] oxygen (alkoxycarbenium ions)[25] and aryl groups (diaryl carbenium ions)[26] are generated and accumulated by low-temperature electrochemical oxidation of corresponding carbamates, α-silylethers and diarylmethanes, respectively in the absence of nucleophiles. In the next step, the accumulated organic cations are subjected to reactions with carbon nucleophiles to give the corresponding carbon–carbon bond formation products.

The first generation of the "cation pool" method uses the direct electrochemical method. Because direct electrochemical reactions take place only on the surface of the electrode, the electrochemical generation of a cation pool on a preparative scale usually takes several hours. Therefore, the applicability of the "cation pool" method using the direct electrochemical method strongly depends on the stability of the cation that is accumulated. Therefore, highly unstable cations might decompose during the course of the accumulation. The "cation pool" method suffers from this problem.

To solve the problem, the "cation flow" method,[6] in which an unstable organic cation is generated in a flow system and is transferred to another location to be used in the subsequent reaction with a nucleophile before it decomposes, has been developed. However, there is another way to solve the problem, which is based on the ex-cell indirect electrochemical method. In this method, a highly reactive reagent is once generated and accumulated electrochemically and is subsequently allowed to react with a precursor to generate an organic cation rapidly. Because the process of generating an organic cation takes place in a homogeneous solution, it could be completed in a short period. Therefore, the decomposition of unstable organic cations might be avoided. For example, the combination of thioacetals[27] as precursors and $ArS(ArSSAr)^+$ as a cation-generating reagent seems to be suitable for rapid generation of alkoxycarbenium ions, because $ArS(ArSSAr)^+$ is considered to be highly thiophilic.

Thus, $ArS(ArSSAr)^+BF_4^-$ is generated by the electrochemical oxidation of ArSSAr (Ar = p-FC_6H_4) in Bu_4NBF_4/CH_2Cl_2 at −78 °C (*step 1*) (Scheme 8). The resulting solution is reacted with a thioacetal **20** to generate the corresponding alkoxycarbenium ion **21** (*step 2*).[28] This process requires only 5 min at −78 °C. In

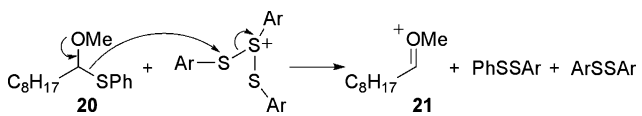


Scheme 8 Indirect cation pool method to generate and accumulate an alkoxycarbenium ion (Ar = *p*-FC_6H_4).

the third step, allyltrimethylsilane (2 equiv.) is added to obtain the final product **22** in 90% yield (*step 3*).[16]

The formation of **21** was confirmed by NMR spectroscopy at –80 °C (Scheme 8). A solution obtained by the reaction of **20** with the electrochemically generated ArS(ArSSAr)$^+BF_4^-$ (Ar = *p*-FC_6H_4) exhibited signals at 9.53 and 4.92 ppm due to the methine proton and methyl protons, respectively (^{1}H NMR), and a signal at 230.6 ppm due to the methine carbon (^{13}C NMR). These chemical shifts were quite similar to those obtained by the direct electrochemical oxidation of $C_8H_{17}CH(OMe)SiMe_3$ (9.55, 4.95 and 231.0 ppm).[25a] Such similarity in chemical shifts indicated that the sulfur-containing by-products, such as PhSSAr and ArSSAr, which should be present in the solution, did not change the nature of alkoxycarbenium ion **21** appreciably.

The detailed mechanism for the reaction of **20** with ArS(ArSSAr)$^+$ (*step 2*) has not been clarified as yet, but **21** seems to be generated according to Scheme 9. Although the possibility of a single electron-transfer mechanism cannot be ruled out, an ionic mechanism seems to be more plausible. In the ionic mechanism, ArS(ArSSAr)$^+$ acted as a thiophilic Lewis acid.[29]

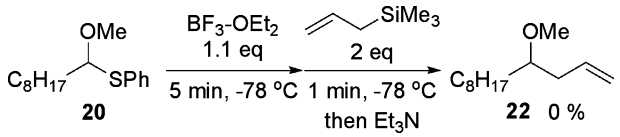


Scheme 9 Plausible reaction mechanism.

The reactions of thioacetals with conventional Lewis acids such as $BF_3{\cdot}OEt_2$ and $SnCl_4$ do not give the corresponding alkoxycarbenium ions under similar conditions. Presumably such Lewis acids are not strong enough to generate alkoxycarbenium ions in a significant concentration. The equilibrium between **20** and **21** lies to **20** in such cases. In fact, Denmark and co-workers could not observe an alkoxycarbenium ion in low-temperature ^{1}H NMR studies of a mixture of an acetal and a conventional Lewis acid, but they observed a Lewis acid–acetal complex.[30]

Much lower reactivity of $BF_3{\cdot}OEt_2$ was confirmed by the following experiments. The reaction of thioacetal **20** with $BF_3{\cdot}OEt_2$ in 5 min followed by treatment with allyltrimethylsilane in 1 min at –78 °C did not give **22** in an appreciable amount (Scheme 10).[31]

As described above, the alkoxycarbenium ion generated by the indirect method exhibited NMR spectra similar to that generated by the direct method.[25a] The thermal stability of the



Scheme 10 Reaction of a thioacetal with $BF_3{\cdot}OEt_2$.

alkoxycarbenium ion generated by the indirect method was found to be also similar to that generated by the direct method. The cation pool generated at –78 °C was allowed to warm to a second temperature. After being kept there for 30 min, the pool was allowed to react with allyltrimethylsilane. Fig. 3, in which the yield of the product **22** is plotted against the temperature, indicates similar stability of the alkoxycarbenium ion generated by the direct method and that generated by the indirect method.[25a]

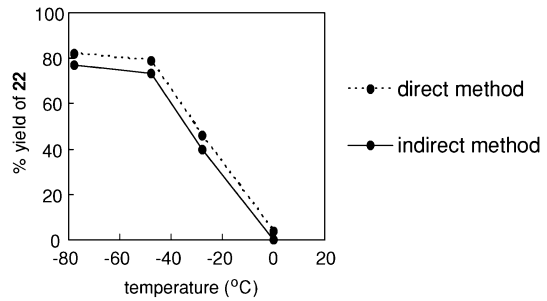
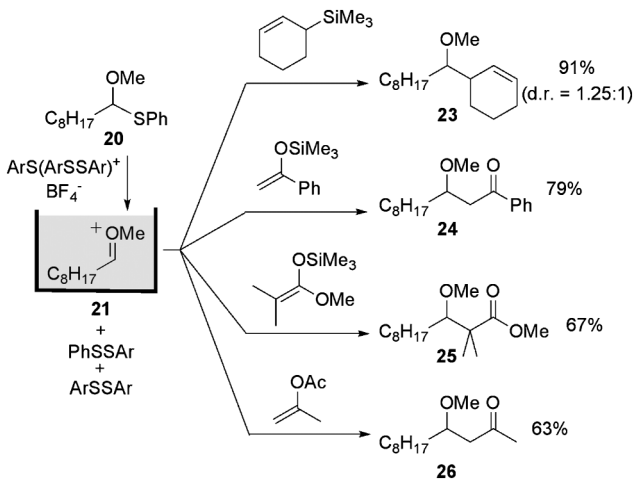


Fig. 3 Thermal stability of alkoxycarbenium ion **21** generated by the direct method and the present indirect method.

Various carbon nucleophiles, such as allylsilanes, enol silyl ethers, ketene silyl acetals and enol acetate are effective to give the corresponding C–C bond formation products (**23–26**) as shown in Scheme 11.



Scheme 11 The reactions of indirectly generated alkoxycarbenium ion pool with various carbon nucleophiles (Ar = *p*-FC_6H_4).

Thioacetals bearing *p*-ClC_6H_4S, *p*-FC_6H_4S and *p*-MeC_6H_4S groups (**27–29**) and aryl and alkyl substituted thioacetals (**30–33**) including cyclic substrates, serve as effective precursors for generation of alkoxycarbenium ion pools (Fig. 4).

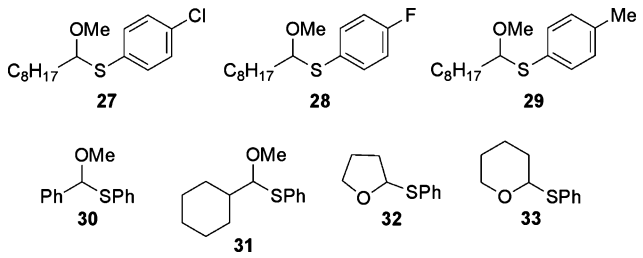
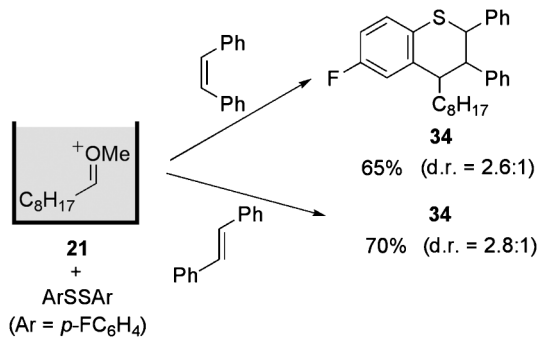


Fig. 4 Precursors of alkoxycarbenium ions used for the indirect cation pool method.

3.3 Reactions with thioacetals followed by reactions with alkenes. Synthesis of thiochromans

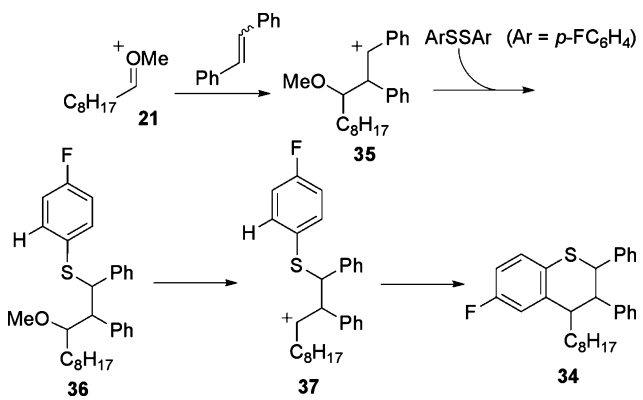
A pool of the alkoxycarbenium ion prepared by the "indirect cation pool" method reacts with stilbene derivatives to give thiochroman derivatives **34** (Scheme 12). In this case ArSSAr, which is present in the solution, participates in the reaction.[32]



Scheme 12 The reactions of the alkoxycarbenium ion pool with stilbenes and ArSSAr (Ar = *p*-FC_6H_4).

The stereochemistry of the present reaction is interesting. The reaction with *cis*-stilbene gave **34** in 65% as a mixture of two diastereomers (d.r. = 2.6 : 1). The reaction of *trans*-stilbene exhibited similar diastereoselectivity (70%, d.r. = 2.8 : 1). The diastereoselectivity indicates that the reaction proceeds by a stepwise mechanism rather than a concerted mechanism.

The mechanism shown in Scheme 13 seems to be reasonable. Alkoxycarbenium ion **21** adds to the carbon–carbon double bond of stilbene to generate cation **35**. Cation **35** reacts with ArSSAr to give intermediate **36**. The elimination of MeO group in **36** generates cation **37**, which cyclizes to give **34**.



Scheme 13 The plausible reaction mechanism.

Various alkoxycarbenium ion pools having Ph, *p*-ClC_6H_4, $PhCH_2CH_2$, and cyclohexyl groups generated and accumulated from the corresponding thioacetals are effective for synthesizing substituted thiochromans (**38–41**) (Fig. 5).

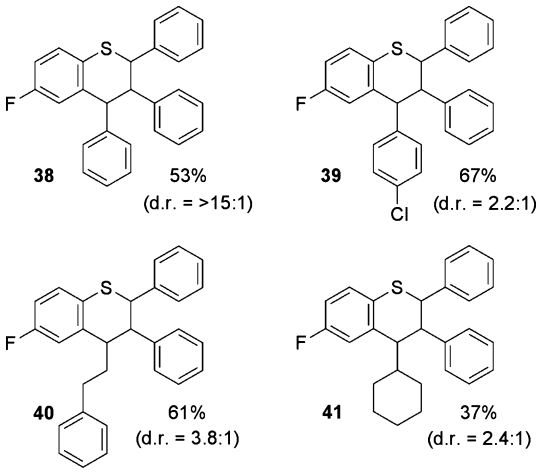


Fig. 5 Synthesis of thiochroman derivatives by the reaction of alkoxycarbenium ion pools with *cis*-stilbene and ArSSAr (Ar = *p*-FC_6H_4).

Because compounds having the thiochroman skeleton show interesting biological activities, several methods for synthesizing the thiochroman derivatives have been developed.[33] For example, Ishibashi and co-workers reported the method based on the reaction of phenylthionium ion with olefins.[34] Ishino and co-workers have developed the method based on intermolecular cycloaddition of α,β-unsaturated aldehydes and thiophenols.[35] Although these literature methods are based on the coupling of two different components, the present method is based on the coupling of three components, an alkoxycarbenium ion, a stilbene derivative and ArSSAr, and therefore the present method serves as a more flexible way for constructing a thiochroman skeleton.

4 Catalytic reactions

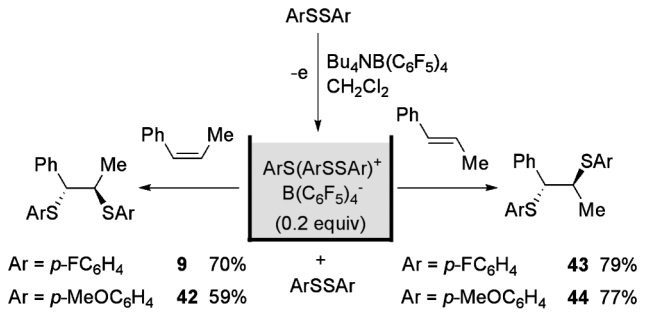
A chain reaction is a sequence of reactions, where a reactive product or by-product causes the next sequence to take place.[36] Radical chain reactions[37] are extensively studied so far. However, cationic chain reactions are not utilized as much in organic chemistry.

Doyle and co-workers reported the first example of cationic chain reactions *via* hydride transfer.[38] The INIFER (INIFER = initiator transfer) method developed by Kennedy and Smith is also recognized as a cationic chain reaction.[39] However, to the best of our knowledge, a cationic chain reaction mediated by organic cations such as "ArS^+" had not been developed when we initiated our studies on reactions using a catalytic amount of "ArS^+" as an initiator and a chain carrier.

4.1 Cation chain reactions of involving cyclization of dienes

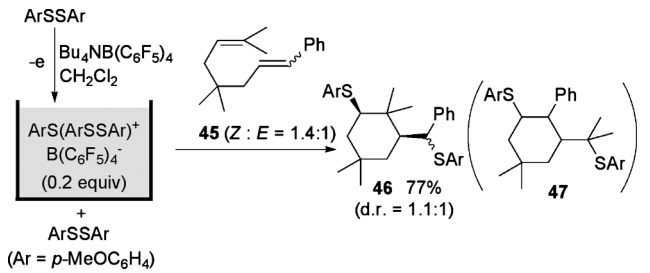
We have already discussed the addition of ArSSAr to alkenes using a *stoichiometric* amount of $ArS(ArSSAr)^+$. The reaction proceeds by adding a soft quenching nucleophile such as Et_3N (Scheme 4). If ArSSAr plays a role as a soft nucleophile, the last step regenerates 'ArS^+', which causes the next sequence to take place (Scheme 5,

soft nucleophile = ArSSAr). If we use $B(C_6F_5)_4^-$ as a counter anion of $ArS(ArSSAr)^+$, this is the case. For example, (*Z*)-1-phenylpropene reacts with ArSSAr in the presence of a catalytic amount of $ArS(ArSSAr)^+B(C_6F_5)_4^-$ to give diarylthio-substituted product (**9** (Ar = *p*-FC_6H_4: 70%), **42** (Ar = *p*-$MeOC_6H_4$: 59%)) (Scheme 14).[40] The reaction of (*E*)-1-phenylpropene also gives the corresponding diarylthio-substituted compounds (**43** (Ar = *p*-FC_6H_4: 79%), **44** (Ar = *p*-$MeOC_6H_4$: 77%)). It is important to note that the use of $B(C_6F_5)_4^-$ as a counter anion is essential for the success of this catalytic process. Therefore, $Bu_4NB(C_6F_5)_4$ as a supporting electrolyte should be used for the electrochemical oxidation of ArSSAr to generate $ArS(ArSSAr)^+B(C_6F_5)_4^-$.



Scheme 14 The reaction of 1-phenylpropenes with ArSSAr in the presence of a catalytic amount of $ArS(ArSSAr)^+B(C_6F_5)_4^-$.

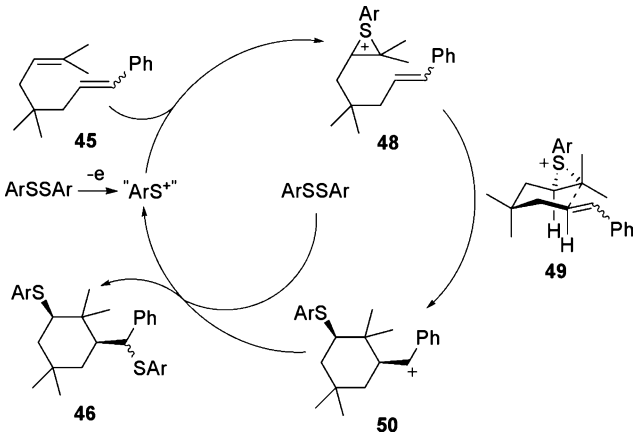
With this information in hand, the cyclization reaction of non-conjugate dienes using a catalytic amount of $ArS(ArSSAr)^+B(C_6F_5)_4^-$ in the presence of ArSSAr has been developed (Scheme 15). For example, 1-phenyl-7-methyl-4,4-dimethylocta-1,6-diene **45** reacted with 0.2 equiv. of $ArS(ArSSAr)^+B(C_6F_5)_4^-$ in the presence of ArSSAr (Ar = *p*-$MeOC_6H_4$). The cyclized product **46** was obtained in 77% yield as a mixture of two diastereomers, although compound **47**, that would be formed *via* another mode of cyclization, was not obtained.[41,42] The observed cyclization mode is consistent with the nucleophilicity parameters reported by Mayr and co-workers.[43] According to their parameters, trialkyl-substituted alkenes are more nucleophilic than β-methylstyrene.



Scheme 15 $ArS(ArSSAr)^+B(C_6F_5)_4^-$ initiated addition of ArSSAr to dienes *via* intramolecular C–C bond formation.

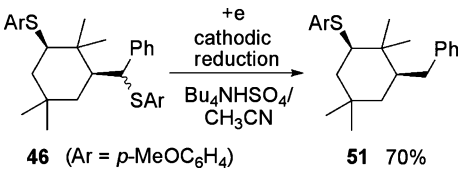
To the best of our knowledge, the present reaction is the first example that the addition of organic disulfide to non-conjugated dienes involves intramolecular carbon–carbon bond formation.

The reaction seems to proceed by a mechanism shown in Scheme 16. The "ArS^+" (= $ArS(ArSSAr)^+$) reacts with the more nucleophilic carbon–carbon double bond in **45** to give episulfonium ion **48**.[18] The other carbon–carbon double bond attacks the episulfonium ion carbon to give cyclized cation **50**, which reacts with ArSSAr to give **46**. The final step regenerates "ArS^+", which causes the next sequence to take place.



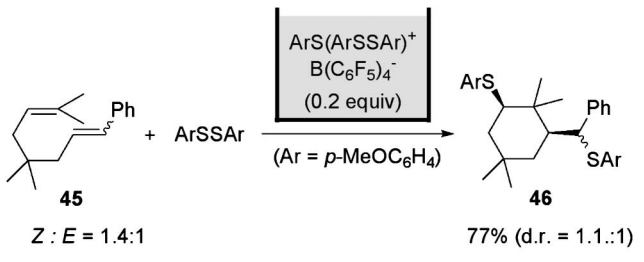
Scheme 16 Mechanism of "ArS^+" (= $ArS(ArSSAr)^+$) initiated addition of ArSSAr to dienes *via* intramolecular C–C bond formation.

The benzylic ArS group in **46** could be selectively removed by the electrochemical reduction,[44] which gave **51** as a single diastereomer (Scheme 17). This stereochemical information suggests that the cyclization proceeds by transition state **49** (Scheme 16), where a carbon–carbon double bond attacks the episulfonium ion from the back side.



Scheme 17 Electroreductive removal of benzylic ArS from product **46** (Ar = *p*-$MeOC_6H_4$).

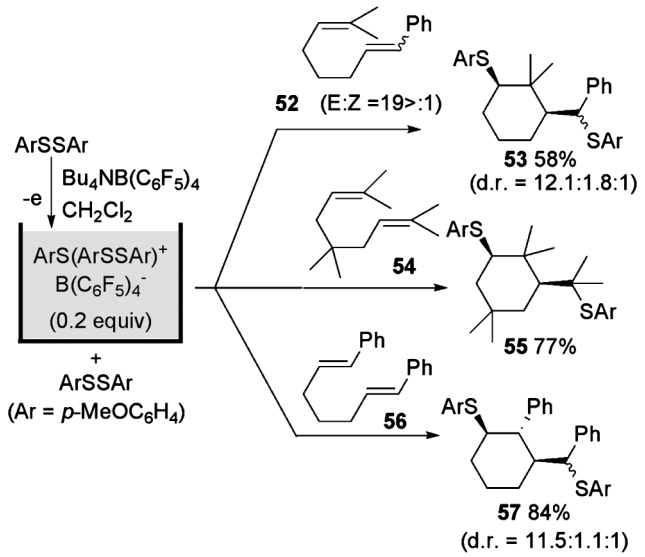
The stereochemistry of the carbon–carbon double bond in **45** does not affect the diastereoselectivity of the cyclization (Scheme 18).



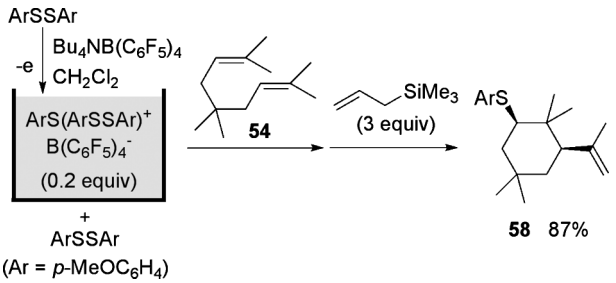
Scheme 18 Stereoselectivity of the reaction of **45** (Ar = *p*-$MeOC_6H_4$).

Other non-conjugated dienes such as **52**, **54** and **56** also reacted in a similar manner to give the corresponding cyclized products (**53**, **55** and **57**) (Scheme 19).

The reaction of a catalytic amount of $ArS(ArSSAr)^+B(C_6F_5)_4^-$ with **54** in the presence of ArSSAr followed by addition of allyltrimethylsilane instead of Et_3N led to the selective formation of olefinic product **58** (Scheme 20). Presumably, "ArS^+" that



Scheme 19 Cation chain reactions of various dienes (Ar = *p*-$MeOC_6H_4$).



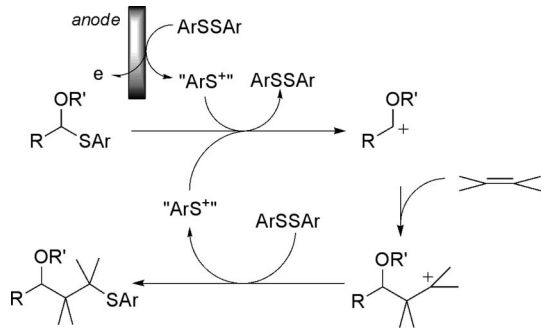
Scheme 20 The reaction of **54** with a catalytic amount of $ArS(ArSSAr)^+B(C_6F_5)_4^-$ followed by adding allyltrimethylsilane (Ar = *p*-$MeOC_6H_4$).

remained in the solution reacted with allyltrimethylsilane to produce highly reactive "Me_3Si^+".[45] "Me_3Si^+" reacted with **55** to cleave the C–S bond generating the tertiary carbocation. β-Proton elimination gave **58**. The resulting proton reacted with allyltrimethylsilane to regenerate "Me_3Si^+".

It is noteworthy that the direct (*in-cell*) electrolysis[3] of a diene in the presence of ArSSAr was also effective to initiate the reaction. Thus, a catalytic amount of electricity was passed through a solution of **45** (0.30 mmol) and ArSSAr (1.0 mmol) (0.20 $Fmol^{-1}$ based on **45**). After the electrolysis, the reaction mixture was stirred for 0.5 h to obtain the cyclized product **46** in 82% yield (d.r. = 1.1 : 1). This method can be applicable to other dienes such as **52**, **54** and **56** to obtain the corresponding cyclized products (**53**, **55** and **57**).

4.2 Cation chain reactions involving cyclization of olefinic thioacetals

In section 3.2, we discussed the formation of alkoxycarbenium ions by the reaction of thioacetals with "ArS^+". The cationic chain reaction involving this process has also been developed.[46] The general reaction scheme is shown in Scheme 21. The reaction of an alkoxycarbenium ion, which is generated by action of a thioacetal with "ArS^+", with an olefin leads to the formation of the second cation.[41] The reaction of the second cation with ArSSAr

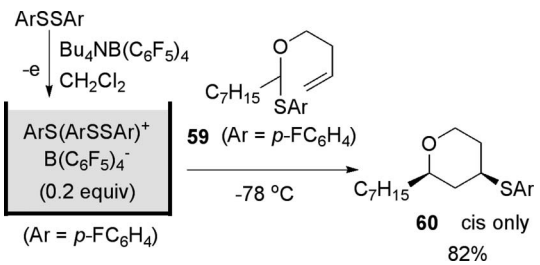


Scheme 21 Cation chain reactions involving the formation of alkoxycarbenium ion.

gives sulfenylated product to regenerate "ArS^+". "ArS^+" would act as an activator of another molecule of the thioacetal. Therefore, the overall reaction should take place with a catalytic amount of "ArS^+".

There are several points to be considered.[31] The formation of the alkoxycarbenium ion takes place quantitatively as we discussed in section 3.2. However, the reaction of the alkoxycarbenium ion with an olefin might be unfavorable because the second cation does not have a neighboring cation stabilizing group such as an oxygen atom, and this step might be a bottleneck of the overall reaction.[47] The last step to form a stable product from the unstable second cation, however, could be energetically favorable, making the overall reaction successful. Another important point to be considered is that the second step could be made entropically favorable by the intramolecularization of the reaction.

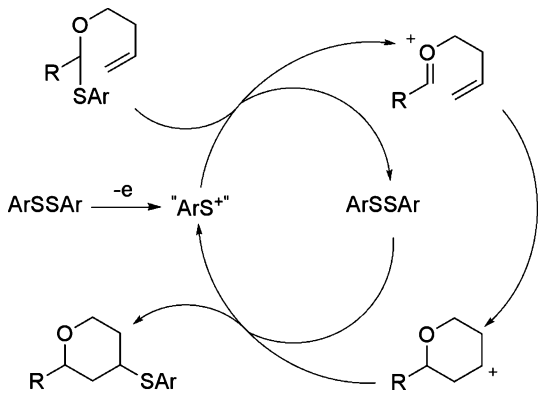
The concept works. For example, treatment of thioacetal **59** (R = C_7H_{15}, Ar = *p*-FC_6H_4) bearing a carbon–carbon double bond with 0.2 equiv. of $ArS(ArSSAr)^+B(C_6F_5)_4^-$ (Ar = *p*-FC_6H_4) at −78 °C led to the formation of cyclized compound **60** (82%) (Scheme 22).[48] In this case, ArSSAr (1.00 mmol) was electrolyzed with 0.04 F mol^{-1} of electricity in $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ at −78 °C, and the resulting solution containing $ArS(ArSSAr)^+B(C_6F_5)_4^-$ (0.04 mmol) and ArSSAr (0.94 mmol) was allowed to react with **59** (0.2 mmol).



Scheme 22 The cyclization of olefinic thioacetal with a catalytic amount of $ArS(ArSSAr)^+B(C_6F_5)_4^-$.

In section 4.1, we discussed cationic chain reactions of dienes involving intramolecular carbon–carbon bond formation, which is net addition of ArSSAr to dienes. In contrast, this reaction is net isomerization. A cationic chain mechanism shown in Scheme 23 seems to be reasonable.

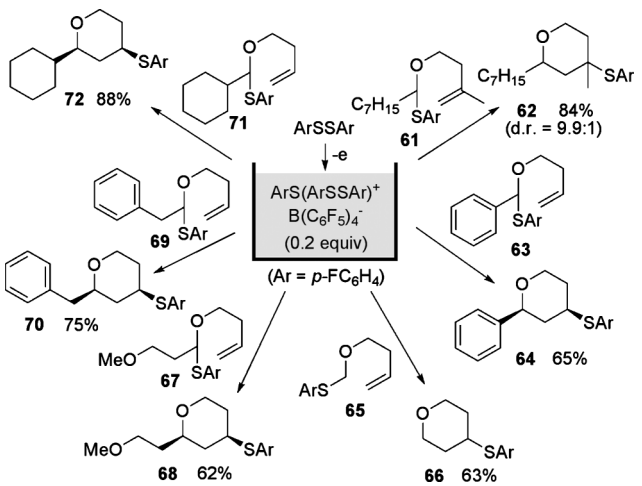
The observed high stereoselectivity (exclusive formation of the *cis* isomer) indicates that the carbon–carbon bond formation and the subsequent reaction of the resulting cation with ArSSAr take



Scheme 23 Mechanism of cationic chain reaction of olefinic thioacetal mediated by "ArS$^+$".

place in somewhat concerted manner. The fact that use of an excess amount of ArSSAr accelerated the reaction is consistent with this mechanism. At higher concentrations of ArSSAr, this step becomes more favorable and hence the overall reaction is accelerated.

The reaction is generally applicable to various olefinic thioacetals bearing a carbon–carbon double bond (**61**, **63**, **65**, **67**, **69** and **71**) to give the corresponding cyclized products (**62**, **64**, **66**, **68**, **70** and **72**) as shown in Scheme 24. The present method is useful to construct a tetrahydropyran ring that serves as a popular structural unit in a variety of biologically interesting molecules.[49] It is also noteworthy that the ArS group could be used for further transformations.



Scheme 24 Intramolecular carbon–carbon bond formation mediated by $ArS(ArSSAr)^+B(C_6F_5)_4^-$.

The *in-cell* method is also effective. The electrolysis of a mixture of an olefinic thioacetal bearing a carbon–carbon double bond and ArSSAr gives the corresponding cyclized product.[3] The reaction is usually conducted by passing a catalytic amount of electricity (0.20 F mol^{-1} based on thioacetal) through a solution of an olefinic thioacetal (0.2 mmol) and ArSSAr (1.0 mmol) in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ at −78 °C under constant current conditions, and after the electrolysis the reaction mixture is stirred for 20 min to obtain the corresponding cyclized product.

5 Conclusion

Low-temperature electrochemical oxidation of ArSSAr generates "ArS$^+$", which has been characterized as $ArS(ArSSAr)^+$ based on spectroscopic studies such as CSI-MS and ^{1}H NMR analysis. The resulting $ArS(ArSSAr)^+$ reacts with carbon–carbon multiple bonds to give diarylthio-substituted compounds and thiofluorinated compounds. $ArS(ArSSAr)^+$ also serves as an effective reagent for rapid generation of alkoxycarbenium ion pools from thioacetals at −78 °C. The resulting alkoxycarbenium ion pools react with carbon nucleophiles to give the corresponding carbon–carbon bond formation products (indirect cation pool method). The reactions of alkoxycarbenium ions with stilbene derivatives give thiochroman derivatives. In addition to these stoichiometric reactions, $ArS(ArSSAr)^+$ also promotes catalytic reactions such as cationic chain reactions. For example, the treatment of dienes with a catalytic amount of $ArS(ArSSAr)^+$ in the presence of ArSSAr leads to net addition of ArSSAr involving intramolecular carbon–carbon bond formation, providing a new type of time and space integration of carbocationic reactions.[50] The reaction of olefinic thioacetals also gives cyclized products. The *in situ* generation of a catalytic amount of "ArS$^+$" is also effective for the cationic chain reactions. These stoichiometric and catalytic reactions demonstrate that the electrochemically generated "ArS$^+$" opens a new aspect of chemistry of organic cations[51] and synthetic transformations utilizing organic cations.

Acknowledgements

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