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Distannane mediated reaction of *N*-acyliminium ion pools with alkyl halides. A chain mechanism involving radical addition followed by electron transfer

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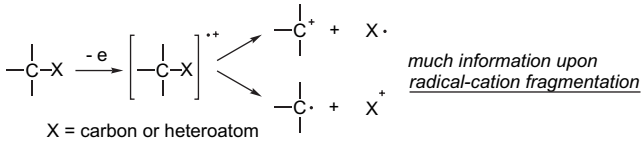
Abstract—Hexabutyldistannane was found to be an effective mediator allowing the reaction of *N*-acyliminium ion pools with alkyl halides. A chain mechanism involving the addition of an alkyl radical generated from an alkyl halide to an *N*-acyliminium ion followed by the one-electron reduction of the resulting radical-cation by distannane was proposed.

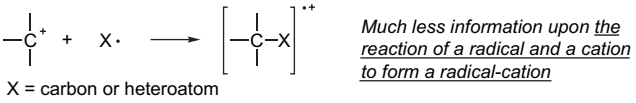
1. Introduction

Radical-cations serve as key intermediates in a variety of electron transfer driven transformations in organic synthesis. For example, one-electron oxidation of organic compounds gives radical-cations, which undergo follow-up reactions. Fragmentation of radical-cations to give either a carbocation or a neutral carbon radical as shown in Scheme 1 is one of the most feasible pathways. Extensive studies have been carried out on fragmentation reactions of radical-cations, which are generated in chemical,[1] electrochemical,[2] and photochemical[3] electron transfer. Schmittel's classification[4] of reactivity patterns of radical-cations is very useful to understand electron transfer driven reactions.[5]

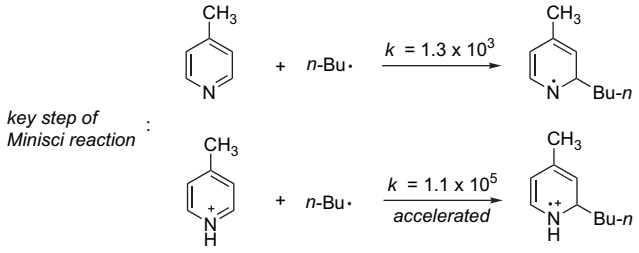


Scheme 1.

Much less information, by contrast, is available for the reverse process: the reaction of a radical and a cation to form a radical-cation (Scheme 2). The Minisci reaction, which involves the addition of nucleophilic radicals, such as alkyl, benzyl, and phenyl radicals, to protonated heteroaromatic rings, serves as an example of the process.[6,7] In this reaction, the rates of the addition to protonated heteroaromatic compounds are much higher than that of the addition to the unprotonated compounds. For example, the addition of an *n*-butyl radical to the protonated picoline is 100 times faster than that to neutral picoline, indicating significant polar effects in the transition state (Scheme 3).[7]



Scheme 2.



Scheme 3.

In the arylative amination of aldehydes promoted by titanium trichloride, a mechanism involving the addition of an aryl radical to the cationic carbon of the protonated imine intermediate has been suggested (Scheme 4).[8]

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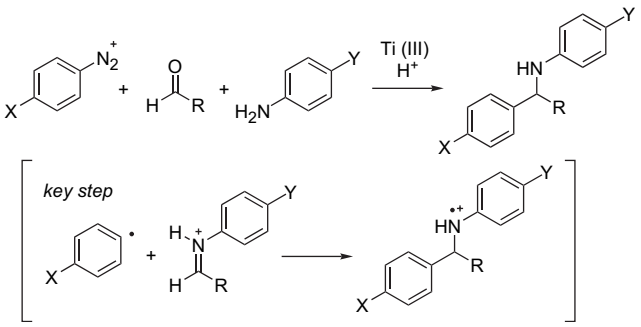
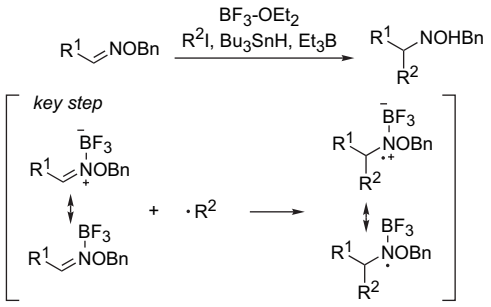


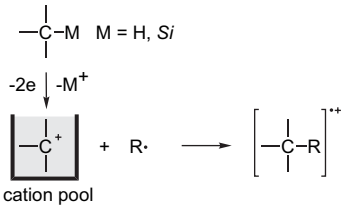
Scheme 4.

It has also been reported that alkyl radical addition to C=N bond is remarkably accelerated by the Lewis acid such as $BF_3 \cdot OEt_2$ (Scheme 5).[9] Lewis acid was suggested to lower the LUMO energy of the radical acceptor and decrease the electron density at the iminyl carbon atom. Similar reactions are possible using imines having an electron-deficient substituent.



Scheme 5.

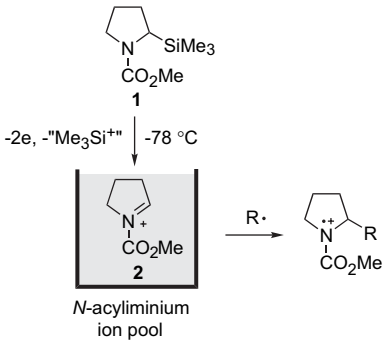
These observations in the literature indicate the importance of electrophilic character of radical acceptors in radical addition and prompted us to investigate the radical addition to *N*-acyliminium ions, which are generated and accumulated by the 'cation pools' method[10] (Scheme 6). In a preliminary communication we have reported that the reaction does take place in the presence of distannane.[11] A chain mechanism involving the addition of an alkyl radical generated from an alkyl iodide to an *N*-acyliminium ion followed by the one-electron reduction of the resulting radical-cation by distannane has been proposed. In this paper we report full details of this study.



Scheme 6.

2. Result and discussion

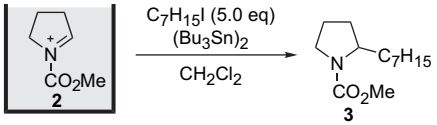
We began our study with surveying appropriate conditions to generate alkyl radicals, which could react with the cation pools. *N*-Acyliminium ion **2**, generated from *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine **1** by low temperature electrochemical oxidation and accumulated in a solution (cation pool), was utilized as a carbocation component (Scheme 7).



Scheme 7.

The triethylborane/O_2 system,[12] which could be widely utilized to generate alkyl radicals from alkyl halides at low temperatures, was unsuccessful; however, we found that the hexabutyldistannane ($Bu_3SnSnBu_3$)/hν system was quite successful. Thus, heptyl iodide reacted with **2** in the presence of $Bu_3SnSnBu_3$ under UV irradiation at −20 °C to afford the corresponding heptylated compound **3** (Table 1, entries 1 and 2). It was surprising that the reaction proceeded even in the dark (entries 3–15), although photo irradiation was well-known to enhance the homolytic cleavage of Sn–Sn bond.[13] A stoichiometric amount of $Bu_3SnSnBu_3$ was necessary to complete the reaction, because the reactions using 0.5 and 0.1 equiv of $Bu_3SnSnBu_3$ led to the formation of **3** in 50 and 10% yields, respectively (entries 8 and 9). The reaction rates strongly depended on temperature. The reaction almost completed around 60 min at −20 °C

Table 1. The addition of heptyl radical to the *N*-acyliminium ion **2**

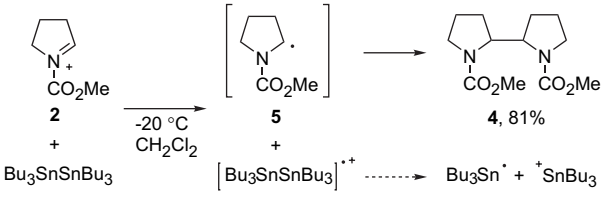


Entry	Temperature (°C)	Time (min)	Condition	$(Bu_3Sn)_2$ (equiv)	Yield (%)
1	−20	60	hν	5.0	64[a]
2	−20	60	hν	2.5	66[a]
3	−20	60	Dark	2.5	77
4	−20	60	Dark	1.5	77
5	−20	60	Dark	1.5	86[b]
6	−20	60	Dark	1.0	72
7	−20	60	Dark	0.5	37
8	−20	180	Dark	0.5	50
9	−20	180	Dark	0.1	10
10	−20	5	Dark	1.5	16
11	−20	30	Dark	1.5	45
12	0	60	Dark	1.5	82
13	−78	60	Dark	1.5	9
14	−20	60	Dark	1.5	82[c]
15	−20	60	Dark	1.5	8[d]

[a] Isolated yield.
[b] Slow addition of distannane.
[c] 2,2,6,6-Tetramethyl-1-piperidinyloxyl (TEMPO) (0.1 equiv) was added.
[d] TEMPO (1.0 equiv) was added.

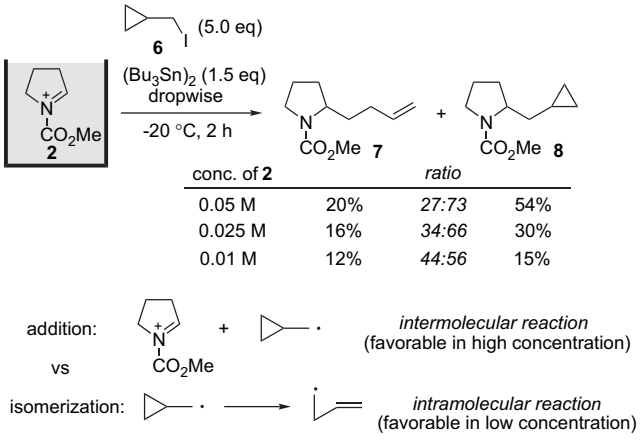
(entries 4, 10, and 11), but only 9% of **3** was obtained at −78 °C (entry 13).

To obtain a deeper insight into the mechanism, the reaction of **2** with $Bu_3SnSnBu_3$ in the absence of alkyl halides was examined at −20 °C. The dimeric product **4** was obtained in 81% yield (a mixture of dl and *meso*) probably via one-electron reduction of **2** by $Bu_3SnSnBu_3$ to form radical intermediate **5** (Scheme 8).[14,15] The radical-cation of $Bu_3SnSnBu_3$ thus formed may undergo Sn–Sn bond cleavage to give a tributylstannyl radical.



Scheme 8.

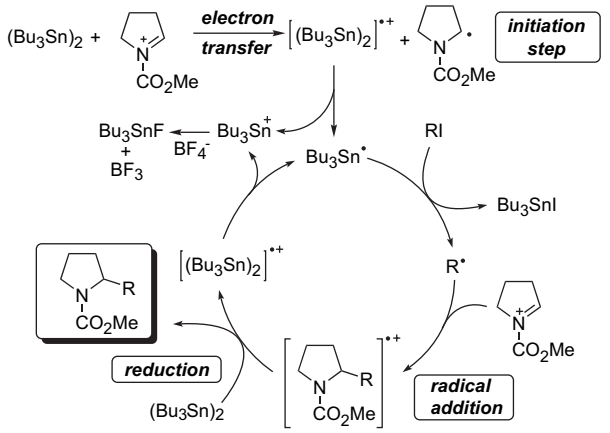
The reaction with cyclopropylmethyl iodide **6** was also examined, because the ring opening of cyclopropylmethyl radical is often used as a radical clock (Scheme 9).[16] The product having the cyclopropyl ring (**8**) was obtained together with the ring-opened product (**7**). Formation of the product containing cyclopropyl ring indicated that the rate of radical addition to *N*-acyliminium ion **2** is comparable to that of ring opening.[17] It is also worth mentioning that the product ratio depends upon the concentration of **2**. At lower concentration of **2**, the relative rate of the isomerization compared to the addition increases, and therefore, the amount of **7** increased with the expense of **8**.



conc. of **2**		*ratio*	
0.05 M	20%	*27:73*	54%
0.025 M	16%	*34:66*	30%
0.01 M	12%	*44:56*	15%

Scheme 9.

On the basis of the above observations, we propose a mechanism described in Scheme 10. The reaction is initiated by one-electron transfer from $Bu_3SnSnBu_3$ to *N*-acyliminium ion **2** to generate the radical-cation of $Bu_3SnSnBu_3$. Cleavage of the Sn–Sn bond leads to the formation of a tributylstannyl radical, together with a tributylstannyl cation, which may react with tetrafluoroborate (electrolyte in electrolysis, see Section 4) to give tributylstannyl fluoride. The tributylstannyl radical abstracts iodine atom from an alkyl iodide to give an alkyl radical. The alkyl radical adds to



Scheme 10.

N-acyliminium ion **2** to generate the radical-cation, which undergoes the electron transfer reaction with $Bu_3SnSnBu_3$ to give the final product together with the radical-cation of $Bu_3SnSnBu_3$. This electron transfer regenerates the radical-cation of $Bu_3SnSnBu_3$. It is important to note that the reduction of the radical-cation by $Bu_3SnSnBu_3$ is faster than the reduction of cation **2** by $Bu_3SnSnBu_3$. This consideration is supported by the DFT calculations.[18] The DFT calculations using *N*-(methoxycarbonyl)dimethylamine as a model compound indicate that the ionization energy of the radical to cation is ca. 6 eV, whereas the ionization of the neutral molecule to radical-cation is 8.44 eV (Fig. 1). It is also noteworthy that the slow addition of $Bu_3SnSnBu_3$ increased the yield of the product (Table 1, entry 5). Moreover, the addition of a catalytic amount of TEMPO (0.1 equiv) as a radical inhibitor did not affect the yield of **3**, but the addition of a stoichiometric amount of TEMPO (1.0 equiv) decreased the yield significantly (8%) (Table 1, entries 14 and 15). These results suggested the participation of $Bu_3SnSnBu_3$ in the initiation step of the reaction, and the radical initiation process took place spontaneously in situ.

Next, we investigated the scope of the present method using other organic halides and cation pools (Table 2). The reaction with an alkyl bromide was rather slow, and

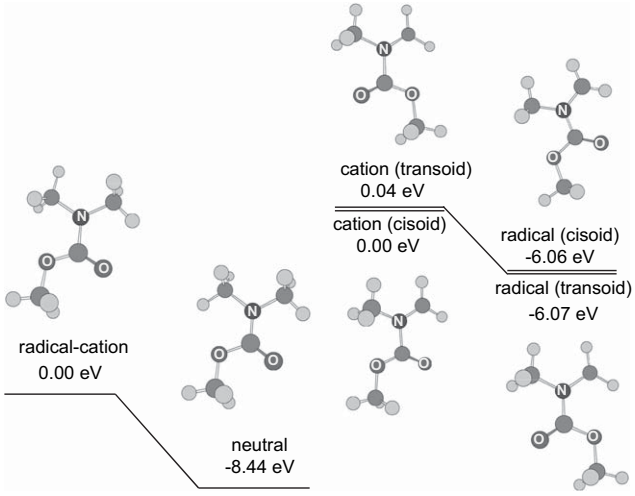
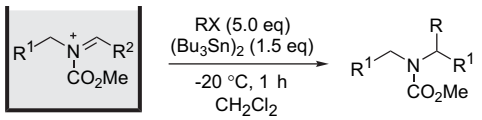
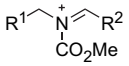
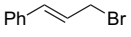
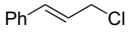
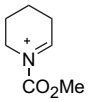
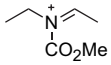


Figure 1. DFT calculations of the radical-cation, neutral molecule, cation, and radical of a model compound.

Table 2. Reactions of organic halides with *N*-acyliminium ion pools in the presence of $Bu_3SnSnBu_3$



	RX	Yield (%)	
		Normal addition	Slow addition
	$C_7H_{15}I$	77	86
	$C_7H_{15}Br$	20	39
	$C_7H_{15}Cl$	1	
	$ClC_7H_{14}I$		81
	c-$C_6H_{11}I$	60	74
	iso-C_3H_7I	43	73
	tert-C_4H_9I	19	
	$PhCH_2Br$	69	77
		3	
		4	
		Complex mixture	
		Complex mixture	
	$C_7H_{15}I$		35
	$C_7H_{15}I$	31	57

the reaction with an alkyl chloride was unsuccessful. The reaction with 1-chloro-6-iodoheptane gave rise to the formation of the corresponding chloroheptylated compound in 81% yield. The slow addition of the distannane was quite effective for the improvement in the yields of the product in the reaction with secondary and tertiary alkyl iodides. Benzyl bromide smoothly reacted with the cation, whereas the reactions using allylic halides were ineffective. The reaction also works for other cyclic and acyclic *N*-acyliminium ions.

3. Conclusion

In summary, we found that $Bu_3SnSnBu_3$ markedly promoted the reactions of alkyl halides with *N*-acyliminium ions. A chain mechanism involving the addition of an alkyl radical to an *N*-acyliminium ion followed by electron transfer reduction of thus formed radical-cation has been suggested. The present observations shed light on a new aspect of the chemistry of radical-cations. It is also noteworthy that the present reaction opens a new possibility for radical-cation crossover-mediated carbon–carbon bond formation.[19]

4. Experimental

4.1. General remarks

^1H and ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (^1H 300 MHz and ^{13}C 75 MHz), Varian MERCURY-plus-400 (^1H 400 MHz and ^{13}C 100 MHz), JEOL A-500 (^1H 500 MHz and ^{13}C 125 MHz), and JEOL ECA-600 (^1H 600 MHz and ^{13}C 150 MHz) spectrometers in $CDCl_3$. EI and CI mass spectra were recorded on JMS-SX102A spectrometer. FAB mass spectra were recorded on JMS-HX110A spectrometer. IR spectra were measured with a SHIMADZU FTIR 1600 spectrometer. GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused silica capillary. Gel permeation chromatography (GPC) was carried out by Japan Analytical Industry's LC-908 equipped with JAIGEL-1H and 2H using $CHCl_3$ as an eluent. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F_{254} plates (thickness 0.25 mm).

4.2. Materials

Dichloromethane was washed with water and distilled from P_2O_5, then removal of a trace amount of acid was carried out by distillation from dried K_2CO_3, and distillate was stored over 4 Å molecular sieves. Trifluoromethanesulfonic acid (TfOH) was purchased from Nacalai and was used without purification. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was purchased from TCI and dried with P_2O_5 under vacuum. All reactions were carried out under Ar atmosphere unless otherwise noted.

4.3. Reactions

4.3.1. Generation of *N*-acyliminium ion pool (2). The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 °C/1 mmHg for 1 h before use) and a platinum plate cathode (40×20 mm). In the anodic chamber was placed a solution of **1** (563.8 mg, 2.8 mmol) in 0.3 M Bu_4NBF_4/CH_2Cl_2 (56 mL). In the cathodic chamber were placed 0.3 M Bu_4NBF_4/CH_2Cl_2 (56 mL) and trifluoromethanesulfonic acid (0.62 mL, 7.0 mmol). The constant current electrolysis (20 mA) was carried out at −78 °C with magnetic stirring until 2.5 F/mol of electricity was consumed.

4.3.2. Methyl 2-heptylpyrrolidinecarboxylate (3). Typical procedure. The electrolysis of **1** was carried out as described above. To the cation pool **2** generated from **1** (56.4 mg, 0.28 mmol) was added 1-iodoheptane (0.20 mL, 1.25 mmol), and hexabutyldistannane (0.19 mL, 0.375 mmol) at −20 °C, and the reaction mixture was stirred for 1 h. Triethylamine were added to the solution at −20 °C, and the resulting mixture was warmed up to room temperature. Solvent was removed under reduced pressure. DBU (1.2 mL, 0.90 mmol) and diethyl ether (10 mL) were added to the residue, and thus obtained solution was quickly filtered through a short column (10 cm) of silica gel. The silica gel was washed with ether (150 mL). The combined solution was concentrated by rotary evaporator, and the crude product thus obtained was purified using flash chromatography (hexane/EtOAc 9:1) and GPC to obtain the title compound (49 mg, 77% by GC analysis): ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.8 Hz, 3H), 1.20–1.36 (m, 11H), 1.63–1.71 (m, 2H), 1.76–1.97 (m, 3H), 3.30–3.49 (m, 2H), 3.67 (s, 3H), 3.73–3.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 23.6, 26.3, 29.4, 29.7, 30.2, 31.9, 34.2, 46.4, 52.1, 57.7, 155.4; IR (neat) 2926.4,

1705.3 cm^{-1}; LRMS (CI) *m/e* 228 (M^++H); HRMS (CI) calcd for $C_{13}H_{26}NO_2$ (M^++H): 228.1964, found: 228.1965.

4.3.3. Methyl 2-cyclohexylpyrrolidinecarboxylate. Typical procedure for slow addition of hexabutyldistannane. The electrolysis of **1** was carried out as described above. To the cation pool **2** generated from **1** (56.4 mg, 0.28 mmol) was added 1-iodocyclohexane (0.16 mL, 1.25 mmol) at −20 °C. Then, hexabutyldistannane (0.19 mL, 0.375 mmol) was added dropwise over a period of 30 min at the same temperature. Then the reaction mixture was stirred for 1.0 h at −20 °C. Triethylamine was added to the solution at −20 °C, and the resulting mixture was warmed up to room temperature. Solvent was removed under reduced pressure. DBU (1.2 mL, 0.90 mmol) and diethyl ether (10 mL) were added to the residue, and thus obtained solution was quickly filtered through a short column (10 cm) of silica gel. The silica gel was washed with ether (150 mL). The combined solution was concentrated by rotary evaporator, and the crude product thus obtained was purified by flash chromatography (hexane/EtOAc 9:1) and GPC to obtain the title compound (33.6 mg, 0.159 mmol, 60% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87–1.09 (m, 2H), 1.09–1.30 (m, 3H), 1.54–1.70 (m, 4H), 1.70–1.90 (m, 6H), 3.21–3.31 (m, 1H) 3.40–3.83 (m, 2H) 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6 and 24.4, 26.2, 26.4, 26.6, 27.3 and 27.7, 30.0, 40.6 and 41.3, 46.7, 52.1, 61.8 and 62.4, 156.0; IR (neat) 2926.4, 1703.4 cm^{-1}; LRMS (CI) *m/e* 212 (M^++H); HRMS (CI) calcd for $C_{12}H_{22}NO_2$ (M^++H): 212.1651, found: 212.1656.

4.3.4. Methyl 2-(4-chlorobutyl)pyrrolidinecarboxylate. Prepared from cation pool **2** generated from **1** (50.3 mg, 0.25 mmol), hexabutyldistannane (0.19 mL, 0.375 mmol), and 1-chloro-4-iodobutane (0.15 mL, 1.25 mmol), and then purified by flash chromatography (hexane/EtOAc 9:1) to obtain the title compound (44.6 mg, 0.203 mmol, 81% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13–2.03 (m, 10H), 3.21–3.50 (m, 2H), 3.53 (t, *J*=6.4 Hz, 2H), 3.66 (s, 3H), 3.71–3.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1 and 24.0, 23.5, 30.0 and 30.6, 32.5, 33.2 and 33.8, 45.0, 46.3 and 46.6, 52.1, 57.0 and 57.7, 155.4; IR (neat) 2955.4, 2872.4, 1701.4 cm^{-1}; LRMS (CI) *m/e* 220 (M^++H); HRMS (CI) calcd for $C_{10}H_{18}ClNO_2$ (M^++H): 220.1104, found: 220.1100.

4.3.5. Methyl 2-isopropylpyrrolidinecarboxylate. Prepared from cation pool **2** generated from **1** (56.4 mg, 0.28 mmol), hexabutyldistannane (0.19 mL, 0.375 mmol), and *iso*-propyl iodide (0.12 mL, 1.25 mmol), and then purified by flash chromatography (hexane/EtOAc 9:1) and GPC to obtain the title compound (20.6 mg, 0.120 mmol, 43% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77–0.94 (m, 6H), 1.69–1.94 (m, 4H), 2.00–2.30 (m, 1H), 3.20–3.30 (m, 1H), 3.54–3.80 (m, 2H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 19.9, 24.8, 26.0, 30.4, 47.4, 52.4, 63.3, 156.2; IR (neat) 2961.1, 1703.4 cm^{-1}; LRMS (CI) *m/e* 172 (M^++H); HRMS (CI) calcd for $C_9H_{18}NO_2$ (M^++H): 172.1338, found: 172.1337.

4.3.6. Methyl 2-benzylpyrrolidinecarboxylate. Prepared from cation pool **2** generated from **1** (56.4 mg, 0.28 mmol), hexabutyldistannane (0.19 mL, 0.375 mmol), and benzyl bromide (0.15 mL, 1.25 mmol), and then purified by flash chromatography (hexane/EtOAc 9:1) and GPC to obtain the title compound (42.4 mg, 0.190 mmol, 69% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69–1.89 (m, 4H), 2.58 (dd, *J*=13.2, 9.6 Hz, 1H), 2.96–3.09 (m, 0.5H), 3.16–3.26 (m, 0.5H), 3.31–3.50 (m, 2H), 3.732 (s, 3H), 3.99–4.14 (m, 1H), 7.12–7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8 and 23.6, 29.0 and 29.9, 39.6 and 40.6, 46.6, 52.2, 58.6 and 59.3, 126.0, 128.2, 129.3, 138.8, 155.4; IR (neat) 2953.4, 1699.5, 702.2 cm^{-1}; LRMS (CI) *m/e* 220 (M^++H); HRMS (CI) calcd for $C_{13}H_{18}NO_2$ (M^++H): 220.1338, found: 220.1337.

4.3.7. Methyl ethyl(1-methyloctyl)aminecarboxylate. The electrolysis of diethylamine carboxylate (52.5 mg, 0.40 mmol) was carried out as described above. To the cation pool **2** thus generated in the anodic chamber, were added 1-iodoheptane (0.33 mL, 2.0 mmol) and hexabutyldistannane (0.30 mL, 0.60 mmol) at −20 °C and the reaction mixture was stirred for 1 h. Triethylamine was added to the stirred solution at −20 °C. Then the mixture was warmed up to room temperature. Solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (150 mL). Then, the crude product thus obtained was purified using flash chromatography (hexane/EtOAc 9:1) and GPC to obtain the title compound (28.6 mg, 0.125 mmol, 31% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J*=6.8 Hz, 3H), 1.00–1.19 (m, 6H), 1.19–1.57 (m, 13H), 3.00–3.29 (m, 2H), 3.69 (s, 3H), 3.91–4.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 15.4 and 16.1, 19.6 and 20.0, 23.1, 27.1, 29.6, 30.0, 32.2, 35.3, 37.4 and 38.2, 52.3, 52.5, 156.9; IR (neat) 2928.3, 1703.4 cm^{-1}; LRMS (CI) *m/e* 230 (M^++H); HRMS (CI) calcd for $C_{13}H_{28}NO_2$ (M^++H): 230.2120, found: 230.2119.

4.3.8. Methyl 2-(3-butenyl)pyrrolidinecarboxylate (7). Prepared from cation pool **2** generated from **1** (56.4 mg, 0.28 mmol), hexabutyldistannane (0.19 mL, 0.375 mmol), and cyclopropylmethyl iodide (227.5 mg, 1.25 mmol), and then purified by flash chromatography (hexane/EtOAc 9:1) and GPC to obtain the title compound (5.5 mg, 0.030 mmol, 11% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30–2.11 (m, 8H), 3.28–3.47 (m, 2H), 3.74–3.88 (m, 1H), 4.88–5.11 (m, 2H), 5.72–5.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9 and 23.8, 29.8 and 30.4, 33.0 and 33.5, 46.2, 52.0, 56.8 and 57.4, 114.5, 138.2, 155.6; IR (neat) 2953.9, 1701.4, 733.0 cm^{-1}; LRMS (EI) *m/e* 183 (M^+); HRMS (EI) calcd for $C_{10}H_{17}NO_2$ (M^+): 183.1259, found: 183.1256.

4.3.9. Methyl 2-(cyclopropylmethyl)pyrrolidinecarboxylate (8). Prepared from cation pool **2** generated from **1** (56.4 mg, 0.28 mmol), hexabutyldistannane (0.19 mL, 0.375 mmol), and cyclopropylmethyl iodide (227.5 mg, 1.25 mmol), and then purified by flash chromatography (hexane/EtOAc 9:1) and GPC to obtain the title compound (22.0 mg, 0.12 mmol, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01–0.16 (m, 2H), 0.37–0.50 (m, 2H), 0.54–0.67 (m, 1H), 1.33–1.46 and 1.49–1.59 (m, 2H), 1.77–2.03 (m, 4H), 3.29–3.51 (m, 2H), 3.67 (s, 3H), 3.80–3.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.3, 5.2, 8.3, 23.5 and 24.3, 30.2 and 30.9, 38.7 and 39.6, 46.6, 52.4, 58.0 and

58.5, 155.8; IR (neat) 2955.3, 1703.4 cm^{-1}; LRMS (CI) *m/e* 184 (M^++H); HRMS (CI) calcd for $C_{10}H_{18}NO_2$ (M^++H): 184.1338, found: 184.1339.

4.3.10. Methyl 2-heptylpiperidinecarboxylate. Prepared from cation pool generated from methyl piperidinecarboxylate (60.3 mg, 0.28 mmol), 1-iodoheptane (0.20 mL, 1.25 mmol), and hexabutyldistannane (0.19 mL, 0.375 mmol), and then purified by flash chromatography (hexane/EtOAc 9:1) and GPC to obtain the title compound (23.7 mg, 0.098 mmol, 35% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.8 Hz, 3H), 1.14–1.33 (m, 10H), 1.33–1.71 (m, 8H), 2.74–2.87 (m, 1H), 3.67 (s, 3H), 3.90–4.06 (m, 1H), 4.14–4.27 (m, 1H); ^{13}C NMR (120 MHz, $CDCl_3$) δ 14.1, 18.9, 22.6, 25.6, 26.2, 28.3, 29.3, 29.5, 29.5, 31.8, 40.0, 50.7, 52.3, 156.3; IR (neat) 2930.2, 2856.9, 1701.4 cm^{-1}; LRMS (CI) *m/e* 242 (M^++H); HRMS (CI) calcd for $C_{14}H_{28}NO_2$ (M^++H): 242.2115, found: 242.2120.

4.3.11. *N*,*N*′-Dimethoxycarbonyl-2,2′-bipyrrolidine (4). This compound was obtained by the reaction of **2** and $Bu_3SnSnBu_3$ in the absence of an alkyl halide. The electrolysis of **1** was carried out as described above. To the cation pool **2** (0.056 M, 5.0 mL, 0.28 mmol) was added hexabutyldistannane (0.19 mL, 0.375 mmol) at −20 °C and the reaction mixture was stirred for 5 h at the same temperature. Triethylamine (0.25 mL) was added to stirred solution at −20 °C and the resulting mixture was warmed to room temperature. Solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (150 mL). Then, the crude product thus obtained was purified using flash chromatography (hexane/EtOAc 9:1) and GPC to obtain the title compound (29.3 mg, 0.114 mmol, 82% yield), which was identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample reported previously.[14]

4.3.12. DFT calculations. The DFT calculations were carried out with model compounds (methyl dimethylamine carboxylate, the radical-cation, radical, and cation derived from it at B3LYP/6-31G(d) level using the Gaussian 98W and 2003W.[18] Geometries were fully optimized. All the optimized geometries were local minima according to the vibration analysis.

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