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# Generation of Carbon Free Radicals by Reduction of the Cation Pool

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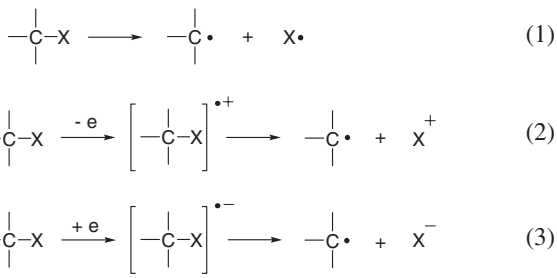
The electrochemical reduction of *N*-acyliminium ions, which were generated by the "cation pool" method, led to the formation of carbon free radicals. Carbon radicals thus generated underwent homo-coupling reactions and the reactions with activated olefins, such as methyl acrylate. In the latter case, a mechanism involving the addition of a carbon radical to the carbon–carbon double bond, followed by one-electron reduction to give carbanions, has been proposed. The present study opens a new possibility for radical-mediated carbon–carbon bond formation based on the reduction of carbocations.

Carbon free radicals are important reactive intermediates in organic chemistry, and are widely utilized in organic synthesis and polymer synthesis.[1] Carbon radicals are usually generated by the homolytic cleavage of the C–X (X = H, halogen, heteroatom, etc.) bond (Eq. 1), but redox-mediated bond cleavage also serves as a useful method for the generation of carbon radicals. For example, one-electron oxidation of neutral compounds having a C–X bond produces radical cation intermediates that decompose to give carbon radicals and $X^+$ (Eq. 2). Carbon radicals can also be generated by one-electron reduction followed by bond cleavage (Eq. 3).

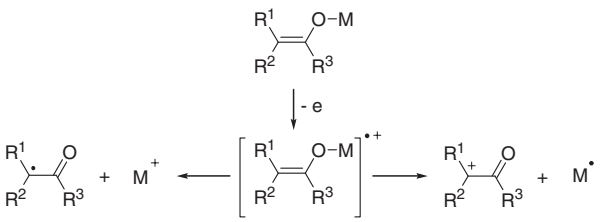


(1)

(2)

(3)

Extensive work by Schmittel revealed that the one-electron oxidation of metal enolates leads to the generation of free radical species (Scheme 1).[2] Metal enolates are easily oxidized to give the corresponding radical cations, which collapse to give carbon radical and metal cation. In some cases the O–M bond cleavage in radical cation leads to the formation of carbocation and metal radical. Although the bond-cleavage mode depends upon the nature of the metal enolates, this reaction serves as a good example that free radicals are generated by the electron transfer-driven bond cleavage.

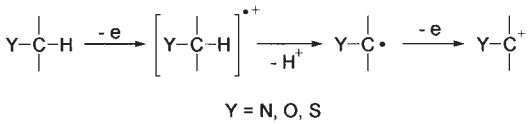


Scheme 1.

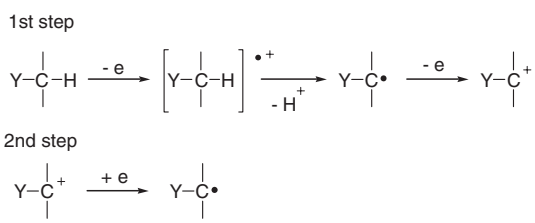
In our previous work, 1,3-diketones were oxidized by the electrochemical method to give the corresponding radicals.[3] The oxidation presumably takes place at the enol form, and the O–H bond cleavage gives the carbon radical adjacent to the carbonyl group. This radical adds to olefins to produce another radical. This radical formation has been successfully applied to oxygenation reactions to form cyclic peroxides.

Oxidative generation, however, often suffers from the problem of over-oxidation. Carbon radicals generated by the decomposition of radical cations are often oxidized to the corresponding carbocations under the conditions. The over-oxidation problem is especially serious for the generation of electron-rich radicals. For example, organic compounds having a heteroatom, such as nitrogen, are easily oxidized to generate the radical cations (Scheme 2, Y = N), and cleavage of $\alpha$ C–H bond produces carbon radicals $\alpha$ to nitrogen. However, these radicals are easily oxidized to give the corresponding iminium ion.[4] Therefore, it is difficult to stop the oxidation at the free radical stage. The oxidation of other heteroatom compounds (Y = O, S) also suffers from a similar over-oxidation problem.[5]

In order to generate free radical species by electron transfer, we envisioned that the following two-step procedure is effective (Scheme 3). In the 1st step, carbocations are generated by the two-electron oxidation of heteroatom compounds. The




Scheme 2.




Scheme 3.

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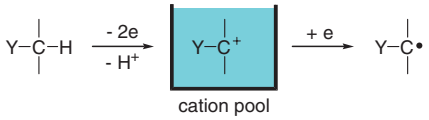
initially formed radical cations collapse to give the carbon radicals, which are further oxidized to give the corresponding carbocations. In the 2nd step, the thus-generated carbocations are reduced to generate free radicals.

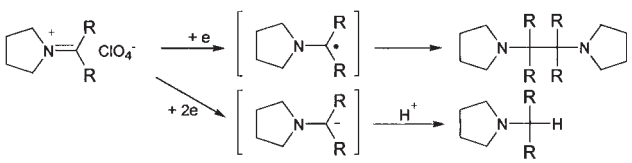
In order to accomplish this two-step transformation, it is necessary to accumulate a carbocation as a solution that is used for the 2nd step. Carbocations, however, are usually trapped immediately after generation in situ by a nucleophile that is present in the reaction medium. This is because carbocations are generally unstable and difficult to accumulate in a solution.[6] Recently, however, we have developed the "cation pool" method, which involves the generation and accumulation of reactive carbocations in the absence of nucleophiles.[7] In the "cation pool" method, carbocations are generated by two-electron oxidation using low-temperature electrolysis, and are accumulated as a solution. Carbocations thus generated are easily characterized by NMR and IR at low temperature. The "cation pool" method has already been successfully applied for *N*-acyliminium ions and alkoxycarbenium ions. Thus, we envisaged that the one-electron reduction of "cation pool" serves as an efficient method for the generation of carbon radicals (Scheme 4).

It is well known that one-electron reduction of carbocation leads to the formation of the corresponding free radical. Pioneering work of Conant revealed that the one-electron reduction of pyridinium ion by low-valent vanadium produces the corresponding carbon radical, which dimerizes to give a homo-coupling product.[8] Savéant has studied the electrochemical reduction of stable iminium salts extensively, and observed two reduction waves in the polarograms (Scheme 5).[9] The first wave corresponds to the one-electron reduction process for which dimerization occurs. This process presumably involves the carbon radical. The second wave is concerned with the formation of the amine by two-electron reduction. When the carbon is substituted by two aromatic groups, stable free radicals are obtained, as indicated by the color of the solution and the EPR spectrum.

Wayner accomplished extensive work on oxidation and reduction potentials of carbon radicals.[10] A modulated photolysis technique was used for radical generation, and phase-sensitive voltammetry was used for their detection. The oxidation potential of the benzyl radical is 0.73 V and the reduction potential is −1.45 V. The oxygen- and nitrogen-substituted radicals exhibit oxidation waves at −0.24 V and −1.03 V, respectively. Arnet studied the redox potentials of the xanthyl system, where the cation and the anion can be generated in the same solvent.[11]




Scheme 4.



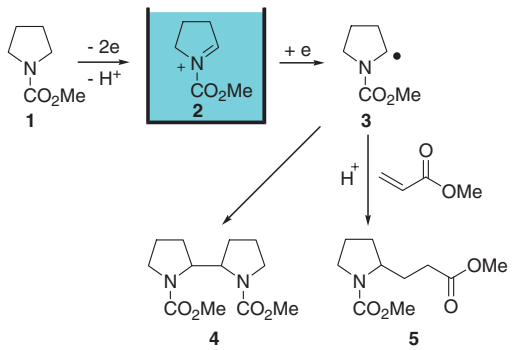

Scheme 5.

The reduction of the cation to the radical takes place at a less negative potential than the reduction of the radical to an anion.

As described above, the conversion of carbocations to carbon radicals can be definitely accomplished by one-electron reduction. Although such a relationship between carbocations and carbon radicals has been well recognized,[12] experimental work has been rather limited to analytical studies on highly stabilized species. The manipulation of such a redox process with complete control still remains as one of the challenging goals of synthetic organic chemistry. Thus, we initiated our project on the reduction of cation pools to generate carbon radicals that can be used for synthetically useful reactions. In a preliminary study, we have already found that the electrochemical reduction of *N*-acyliminium ion **2** generated from **1** gave homo-coupling product **4**, presumably via free radical **3** (Scheme 6).[13] We also revealed that the reduction of **2** in the presence of methyl acrylate and an excess amount of proton gave the coupling product **5**. A mechanism involving the addition of radical **3** to the carbon–carbon double bond of methyl acrylate was proposed. Herein, we report on the full details of this study.

## Results and Discussion

**Reduction Potential of Cation Pool.** We first studied the redox behavior of the *N*-acyliminium ion, which is generated by the "cation pool" method, using cyclic voltammetry. The reduction potentials were determined in $Bu_4NBF_4/CH_2Cl_2$ using a glassy carbon electrode. A $Ag/Ag^+$ ($CH_3CN$) electrode was used as a reference electrode. The *N*-acyliminium ion **2** was generated by the anodic oxidation of *N*-(methoxycar-




Scheme 6.

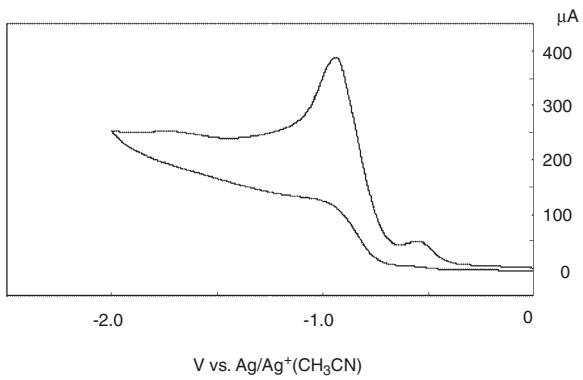
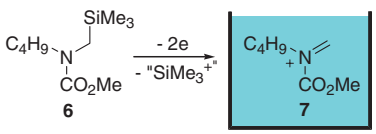



Fig. 1. Cyclic voltammogram for the reduction of *N*-acyliminium ion **2**.

bonyl)pyrrolidine **1** as a precursor in $Bu_4NBF_4/CH_2Cl_2$ at −78 °C, and accumulated as a solution. As shown in Fig. 1, *N*-acyliminium ion **2** exhibited a major reduction wave at $E_p = -0.85$ to −0.90 V, although a small peak was observed at −0.5 V, presumably due to the reduction of an impurity that is difficult to remove. It should be noted that this reduction potential is much less negative than that reported for the reduction of the *N*,*N*-dialkyliminium ion ($E_{1/2} = -1.95$ V).[9] A significant positive shift of the reduction potential seems to be attributed by the electron-withdrawing effect of methoxycarbonyl group on the nitrogen atom.

*N*-Acyliminium ion **7** was generated by the low-temperature oxidation of **6**, which has a silyl group as an electroauxiliary[14] (Scheme 7). Electroauxiliary is a group that facilitates electron transfer and controls the follow-up chemical processes. *N*-Acyliminium ion **7** exhibited a reduction wave at a less negative potential (−0.75 V) than that of **2**, as shown in Fig. 2.

**Preparative Electrochemical Reduction of Cation Pool in the Absence of Radical Acceptor. Homo-Coupling Reaction:** Next, we examined the preparative electrochemical reduction of the cation pool in the absence of a radical acceptor. The electrochemical reduction of acyliminium ion **2** generated from **1** was carried out under a constant-current condition at −78 °C in a divided cell equipped with a carbon-rod anode. As expected, the homo-coupled product **4** was obtained as shown in Scheme 8.




Scheme 7.

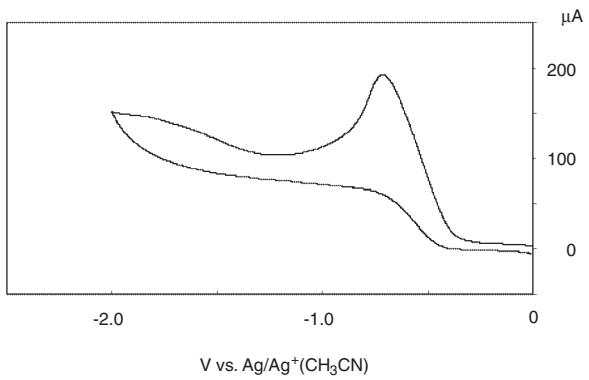
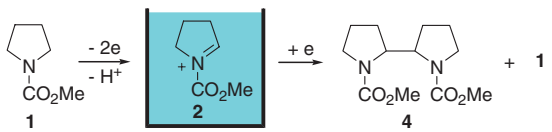



Fig. 2. Cyclic voltammogram for the reduction of *N*-acyliminium ion **7**.

At first, the effect of the electrode material was examined (Table 1). The use of a carbon-rod cathode gave rise to the formation of **4** in 31% yield together with **1**, which was the same as the starting material for the generation of the cation pool **2**, in 13% yield (run 1). Because the solution of **2** did not contain **1** (conversion of **1** was ca. 100%), **1** was definitely produced during the course of the electrochemical reduction. The yield slightly increased when the cathode was switched to carbon felt (run 2). In order to facilitate the anodic reaction, some compounds that might play the role of a substrate for anodic oxidation seemed to be needed. Thus, THF, which is easily oxidized and should not affect cathodic reduction, was added as a substrate for oxidation in the anodic chamber. This caused a slight increase in the yield of **4** (run 3), although it was not clear that THF was oxidized anodically. The increase in the amount of electricity did not affect the yield of **4** significantly (run 4).

The use of a platinum cathode suppressed the formation of **1** (runs 5, 6), although the reason is not clear at present. In any case, the formation of a significant amount of **1** is disadvantageous from a synthetic point of view. Therefore, the use of a platinum electrode seems to be better from a synthetic point of view. With a platinum electrode, the yield of **4** could be improved up to 75% (a mixture of two diastereomers (51:49)) by increasing the electricity (run 7), although **1** was also formed in 7% yield. In this case, the excess electricity may be consumed for the reduction of protons generated during the course of the anodic oxidation of **1**.

The present result implies that the one-electron reduction of **2** produced carbon-centered radical **3**, which homo-coupled to give **4** (Scheme 9). It is also reasonable to consider that radical **3** reacts with **2** to give a dimeric radical cation **8**, the one-electron reduction of which gives a homo-coupled product **4**. It seems to be difficult, however, to distinguish these two mechanisms experimentally at present. Another possibility to be considered is that the two-electron reduction of *N*-acyliminium ion

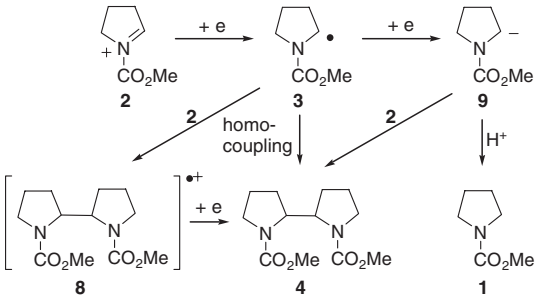



Scheme 8.

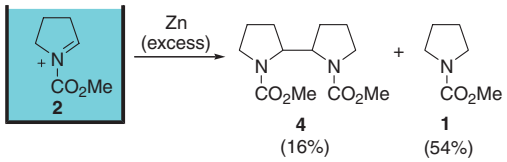
Table 1. Electrochemical Reduction of **2**[a)]

| Run | Cathode | Additive to anodic solution | Electricity /F mol$^{-1}$ | Yield of **4** | Yield of **1** |
|---|---|---|---|---|---|
| 1 | C (rod) | — | 1.25 | 31 | 13 |
| 2 | C (felt) | — | 1.25 | 47 | 18 |
| 3 | | THF (10 equiv) | 1.25 | 62 | 13 |
| 4 | | THF (10 equiv) | 1.75 | 65 | 22 |
| 5 | Pt (plate) | — | 1.25 | 49 | 0 |
| 6 | | THF (10 equiv) | 1.25 | 47 | 0 |
| 7 | | THF (10 equiv) | 2.0 | 75 | 7 |

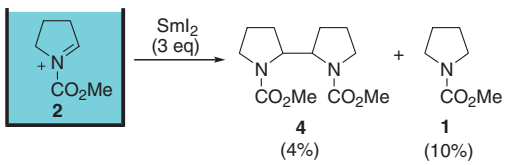
a) The cathodic reduction was usually carried out with 0.4 mmol scale with 8 mA of electric current.



Scheme 9.



Scheme 10.

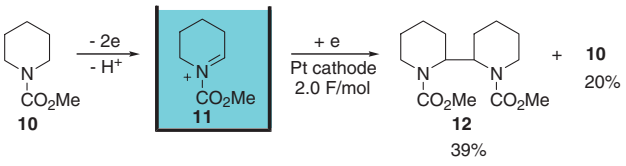


Scheme 11.

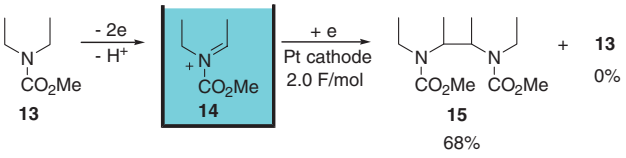
**2** took place to give carbanion **9**, which reacted with the original *N*-acyliminium ion **2** to produce the dimer. Simply reduced product **1** was probably formed via protonation of the carbanion **9**. Presumably, two-electron reduction also took place with a carbon cathode to give a significant amount of **1**, whereas with a platinum cathode one-electron reduction is more favorable to give the homo-coupled product **4** selectively.

The reduction of the *N*-acyliminium ion **2** with chemical reducing agents was also studied.[15] When zinc powder was used as a reducing agent, **1** was obtained as the major product (54%) together with the homo-coupled product **4** (16%) (Scheme 10). Two-electron reduction of the acyliminium ion seemed to take place predominantly to produce the corresponding carbanion **9**, which is trapped by a proton in the reaction media to give **1**. When $SmI_2$ was used as a reducing agent, **1** was also formed as the major product (10%) together with a small amount of **4** (4%), although the material balance was not good (Scheme 11). These results suggest that two-electron reduction is the major pathway in the chemical reduction, whereas one-electron reduction is predominant in electrochemical reduction. It is reasonable to consider that metal ions in the chemical reduction system coordinate to stabilize carbanion **9** and facilitate the two-electron reduction process, although the detailed mechanism is not clear at present.

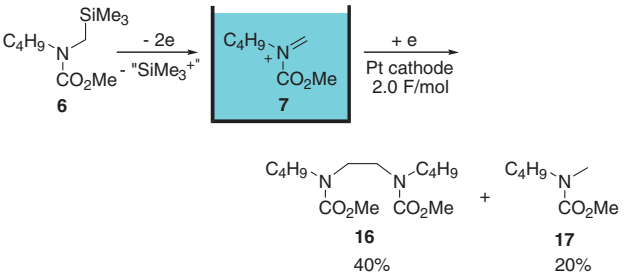
We next examined the electrochemical reductive homo-coupling of other *N*-acyliminium ions. The electrochemical reduction of *N*-acyliminium ion **11** generated from the six-membered ring carbamate **10** also gave the corresponding homo-coupled product **12** in 39% together with a simply reduced product **10** (20%) (Scheme 12). The reduction of **14** generated from acyclic carbamate **13** also proceeded smoothly to give homo-coupled product **15** in 68% yield (Scheme 13). In this case, the corresponding simply reduced product was not obtained. The cathodic reduction of *N*-acyliminium ion **7** generated from a silyl-substituted carbamate **6** was also carried out to obtain the homo-coupled product **16** in 40% yield together with a simply reduced product **17** in 20% yield (Scheme 14).



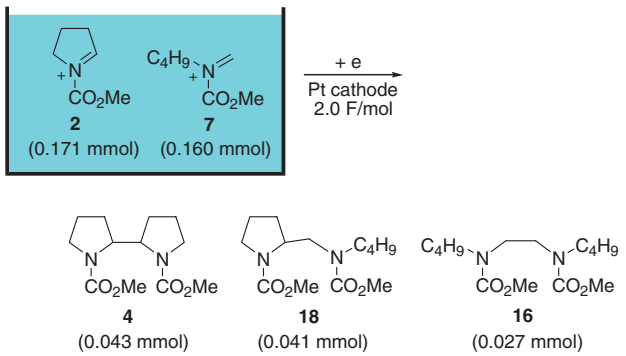
Scheme 12.



Scheme 13.



Scheme 14.



Scheme 15.

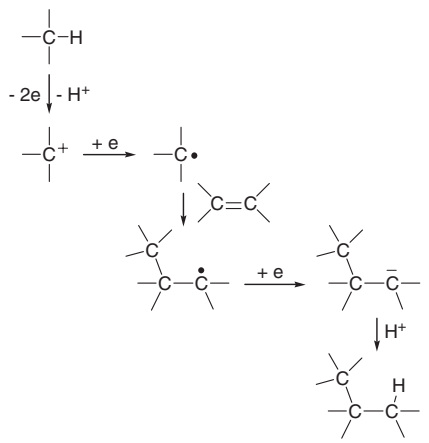
In order to obtain a deeper insight into the reaction mechanism, a mixture of two cation pools (**2** and **7**) was reduced electrochemically (Scheme 15). Although the reduction potential ($E_p = -0.75$ V) of **7** is slightly less negative than that of **2**, the reduction took place almost non-selectively to give a mixture of three coupling products (**4**, **16**, and **18**). The result is consistent with the mechanism involving radical coupling, but mechanisms involving radical–cation coupling and anion–cation coupling are also possible.

**Cathodic Reduction of Cation Pool in the Presence of Radical Acceptor.** Next, we focus on the reduction of the cat-

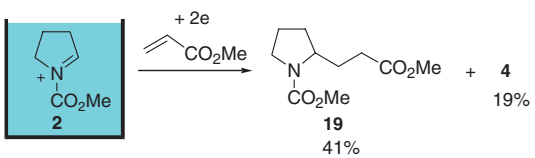
ion pool in the presence of radical acceptors.[16] The radical that is formed by one-electron reduction of the cation is expected to add to a carbon–carbon double bond, as shown in Scheme 16. We also expected that the resulting radical undergoes a subsequent one-electron reduction to generate a carbanion species, which is trapped by a proton. The overall transformation serves as a formal addition reaction of C–H to C=C.[17]

Thus, we examined the electrochemical reduction of the *N*-acyliminium ion pool (**2**) in the presence of methyl acrylate (5 equiv) in order to achieve the addition of the radical intermediate to the carbon–carbon double bond (Scheme 17).[18] THF (10 equiv) was added to the anodic solution in order to facilitate the anodic reaction. We first examined the effect of the cathode material. As the anode, a carbon rod was used throughout this study. Surprisingly, a carbon-felt cathode is much better than a platinum-plate cathode. When a platinum cathode was used, the desired product **19** was obtained in 41% yield together with homo-coupled product **4** in 19% yield. The use of a platinum cathode resulted in the formation of a significant amount of homo-coupled product. The use of a zinc rod cathode gave rise to lower yields of **19** (8%) and **4** (6%).

The following mechanism seems to be reasonable (Scheme 18). The one-electron reduction of acyliminium ion **2** gives radical **3**. Because **3** is a rather electron-rich radical, it adds to the electron-deficient carbon–carbon double bond of methyl acrylate (path A). The resulting carbon radical (**20**) is an electron-deficient radical, and is therefore easily reduced to give the corresponding carbanion (**21**), which is trapped by a proton to give the final product (**19**). Another possibility to consider is the pathway via carbanion **9** (path B). Carbanion **9** attacks the carbon–carbon double bond of methyl acrylate to give carbanion **21**.



Scheme 16.

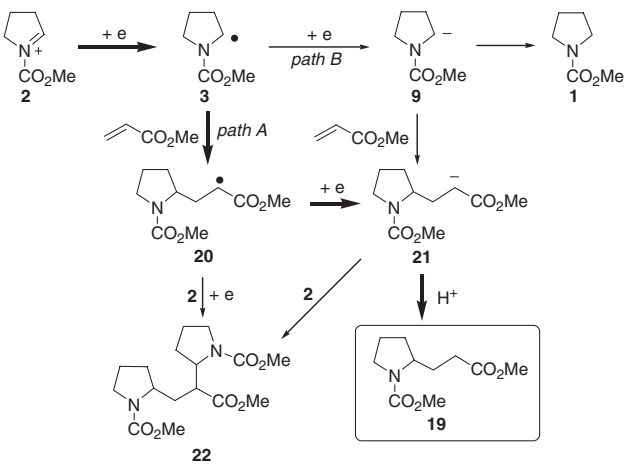


Scheme 17.

This reaction, however, suffered from the formation of a 2:1 coupling product (**22**) (20–40% yield), which might be produced by the reaction of **21** with **2**. A mechanism involving the reaction of radical **20** with **2** to give **22** seems to be less likely, because **20** is an electron-deficient radical. The addition of such an electron-deficient radical to an electron-deficient carbon–nitrogen double bond does not take place easily.

The problem concerning the formation of **22** was overcome by the addition of trifluoromethanesulfonic acid (TfOH) as a proton source (Table 2). Prior to a study of the reduction in the presence of TfOH, we confirmed that the addition of TfOH did not affect the *N*-acyliminium ion **2** appreciably by NMR spectroscopy. Thus, the reaction was carried out with 50 equiv of TfOH. The amount of **22** produced was negligible, and the yield of **19** increased up to 88%. Presumably, the carbanion intermediate **21** was selectively trapped by a proton to give **19**. As for the amount of the radical acceptor, the use of 5 equiv of methyl acrylate gave the best result.

As described previously, the two-electron reduction of **2** to



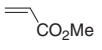
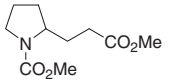
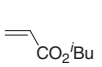
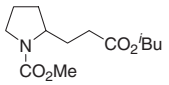
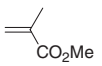
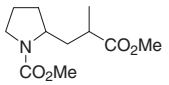
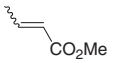
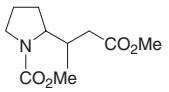
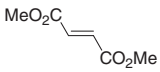
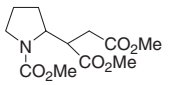
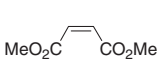
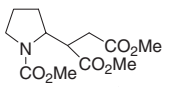
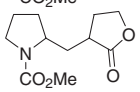
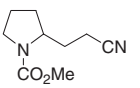
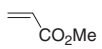
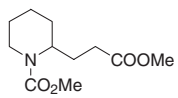
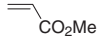
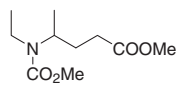
Scheme 18.

Table 2. Electrochemical Reduction of **2** in the Presence of Methyl Acrylate[a)]

| Run | TfOH /equiv | Methyl acrylate /equiv | Products[b)]/% | | | |
|---|---|---|---|---|---|---|
| | | | **19** | **4** | **22** | **1** |
| 1 | 0 | 5 | 34 | 11 | 28 | 2 |
| 2 | 10 | 5 | 66 | 3 | 17 | 1 |
| 3 | 50 | 2 | 78 | 0 | 0 | 4 |
| 4 | 50 | 5 | 88 | 0 | 0 | 0 |
| 5 | 50 | 8 | 83 | 0 | 0 | 0 |

a) The reactions were carried out in a divided cell using a carbon felt cathode. 0.01 M cation pool was used. b) GC yields.

Table 3. Redox-Mediated Coupling of Carbamates and Activated Olefins via Cation Pool[a)]

| Carbamate | Activated olefin | Product | Yield[b)]/% |
|---|---|---|---|
|  |  |  | 84 (88) |
| |  |  | 75 |
| |  |  | 77<br>dr = 59:41[c)] |
| |  |  | 32<br>dr = 64:36[c)] |
| |  |  | 41[d)]<br>dr = 48:52[c)] |
| |  |  | 39<br>dr = 48:52[c)] |
| |  |  | 71<br>dr = 73:27[c)] |
| |  |  | 12 |
|  |  |  | 53 |
|  |  |  | 63 |

a) The reaction was carried out with 5–8 equiv of an activated olefin and 50 equiv of TfOH. The carbon felt was used as the anode for the generation of the cation pool and as the cathode for the subsequent reduction of the cation pool (0.01 M). b) Isolated yields. Yield in parentheses was GC yield. c) Diastereomer ratio. d) 0.05 M cation pool was used.

generate carbanion **9**, followed by nucleophilic addition to the carbon–carbon double bond to give **19**, might be an alternative pathway (path B), but this possibility is denied by the fact that the yield of simply reduced product **1** did not increase by the addition of a large excess amount of TfOH, which should trap the carbanion **9** to give **1** (Table 2).

The present reaction with activated olefins is generally applicable to other cyclic (**1** and **10**) and acyclic (**13**) carbamates, as shown in Table 3. The corresponding coupling product was obtained in good yields. As an activated olefin, acrylates, methacrylate, crotonate, fumarate, maleate, and $\alpha,\beta$-unsaturated lactone were effective, although the yields of the cross-coupled products depended on the structure of the substrates. The use of acrylonitrile gave the desired coupling product, but the yield was very low. The use of methyl vinyl ketone and other $\alpha,\beta$-unsaturated ketones resulted in the formation of complex mixtures, although the reason is not clear at present.

## Conclusion

In conclusion, the research described above demonstrates that free radical species can be generated by the electrochemical reduction of a "cation pool" and that they are utilized for homo-coupling reactions and coupling reactions with activated olefins. The present work establishes a new strategy for radical-mediated carbon–carbon bond formation, which opens new opportunities to manipulate reactive carbon species using redox processes in organic synthesis.

## Experimental

**General Remarks.** GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused-silica capillary. $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 2000 spectrometer or a JEOL $\alpha$-500 spectrometer with $Me_4Si$ as an internal standard, unless otherwise noted. NMR spectra of the carbamates were usually very broad and sometimes separated into two signals due to their rotamers. Especially in cases where two diastereomers exist, the $^{13}$C NMR spectra were complicated and a few signals were occasionally missing. Mass spectra were obtained on a JEOL JMS SX-102A mass spectrometer. Elemental analyses were carried out at the Kyoto University Elemental Analysis Center. IR spectra were measured with a SHIMADZU FTIR 8100 spectrometer. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel $F_{254}$ plates (thickness 0.25 mm). Gel permentation chromatography (GPC) was carried out on a Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using $CHCl_3$ as an eluant. All reactions were carried out under an Ar atmosphere, unless otherwise noted.

**Materials.** Tetrabutylammonium tetrafluoroborate was purchased from TCI and dried at 50 °C/1 mmHg overnight before use. Dichloromethane was washed with water, distilled from $P_2O_5$, redistilled from dried $K_2CO_3$ to remove a trace amount of acid, and stored over molecular sieves 4A. THF was purchased from Kanto as a dehydrated solvent.

**Cyclic Voltammetry.** The cyclic voltammetry of cation pools was carried out with BAS100B in $Bu_4NBF_4/CH_2Cl_2$ at −20 °C. A glassy carbon electrode was used as the cathode and a Pt wire electrode was used as the anode. $Ag/Ag^+$ ($CH_3CN$) was used as the reference electrode. The scan rate was 100 mV/s.

***N*,*N*′-Bis(methoxycarbonyl)-2,2′-bipyrrolidine (4). Typical Procedure of Homo-Coupling:** The electrochemical homo-coupling was carried out in an H-type divided cell (4G glass filter) having two chambers: chamber A equipped with a carbon felt electrode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 °C/1 mmHg for 2 h before use) and a platinum plate electrode (30 mm × 25 mm); chamber B equipped with a platinum plate electrode (30 mm × 25 mm) and a carbon-rod electrode (Touhou Tanso Kougyou ER-38H, diameter 7 mm). In chamber A were placed **1** (52.6 mg, 0.407 mmol) and 0.3 M $Bu_4NBF_4/CH_2Cl_2$ (8.0 mL). In chamber B were placed trifluoromethanesulfonic acid (169.8 mg, 1.13 mmol) and 0.3 M $Bu_4NBF_4/CH_2Cl_2$ (8.0 mL). Constant-current electrolysis (8 mA) was carried out by using a carbon-felt electrode in chamber A as an anode and a platinum plate electrode in chamber B as a cathode at −78 °C with stirring until 2.5 F/mol of electricity was consumed. Thus, the cation pool of **2** was generated. After the anodic oxidation of **1** was completed, to the solution in chamber B was added THF (275.5 mg, 3.82 mmol), which would serve as a substrate for oxidation during the reduction of **2** in chamber A. Constant-current electrolysis (8 mA) was carried out by using the platinum plate electrode in chamber A as a cathode and the carbon-rod electrode in chamber B as an

anode at −78 °C with stirring until 2.0 F/mol of electricity was consumed. The reaction mixture in chamber A was transferred to a flask and the solvent was removed under reduced pressure. 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 (300 mL). The GC analysis of the combined filtrate indicated that **4** was produced in 75% yield. Purification with flash chromatography (hexane/EtOAc 2:1 to 1:2) gave the two diastereomers (diastereomer ratio was 51:49). **a**: GC ($t_R$ 11.5 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.33 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.58–2.10 (m, 8H), 3.21–3.44 (m, 4H), 3.69 (s, 6H), 3.86–4.26 (m, 2H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 22.8 and 23.0 and 23.3 and 23.5, 26.6 and 27.6 and 28.0 and 28.8, 46.4 and 47.3, 52.2, 58.3 and 59.4 and 59.8 and 60.4, 155.9 and 156.0 and 156.7; IR (KBr) 1694, 1377, 1113 cm$^{-1}$; LRMS (EI) *m/e* 256 ($M^+$), 128 ($M^+ - C_6H_{10}NO_2$); HRMS (EI) calcd for $C_{12}H_{20}N_2O_4$ 256.1423, found 256.1422; Anal. Calcd for $C_{12}H_{20}N_2O_4$: C, 56.23; H, 7.87; N, 10.93%. Found: C, 56.02; H, 7.90; N, 10.65%. **b**: GC ($t_R$ 11.2 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.23 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.57–2.20 (m, 8H), 3.21–3.59 (m, 4H), 3.68 (s, 6H), 3.80–4.13 (m, 2H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 22.5 and 22.7 and 23.2 and 23.5, 27.6 and 28.4 and 28.5 and 28.7, 46.0 and 46.5 and 46.7 and 47.0, 52.0 and 52.2 and 52.4, 58.8 and 59.1 and 59.5 and 59.7, 155.5 and 155.6 and 155.8 and 155.9; IR (KBr) 1690, 1383, 1111 cm$^{-1}$; LRMS (EI) *m/e* 256 ($M^+$), 128 ($M^+ - C_6H_{10}NO_2$); HRMS (EI) calcd for $C_{12}H_{20}N_2O_4$ 256.1423, found 256.1419.

***N,N′*-Bis(methoxycarbonyl)-2,2′-bipiperidine (12).** Prepared from the cation pool generated from methyl 1-piperidinecarboxylate (**10**) (58.4 mg, 0.408 mmol), and purified by flash chromatography (hexane/EtOAc 5:1 to 2:1) to give the two diastereomers (total 22.6 mg, 39%, diastereomer ratio was 42:58). **a**: GC ($t_R$ 15.8 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.25 (hexane/EtOAc 3:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.24–1.96 (m, 12H), 2.67–2.88 (m, 2H), 3.69 (s) and 3.71 (s) (total 6H), 3.93–4.20 (m, 2H), 4.49–4.79 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 18.9 and 19.0 and 19.2 and 19.3, 24.4 and 24.6 and 24.7 and 24.9, 25.1 and 25.4, 39.5 and 39.8, 47.7 and 47.7 and 48.1 and 48.1, 52.6, 156.1 and 156.2; IR (KBr) 1685, 1441, 1380 cm$^{-1}$; LRMS (EI) *m/e* 284 ($M^+$), 142 ($M^+ - C_7H_{12}NO_2$); HRMS (EI) calcd for $C_{14}H_{24}N_2O_4$ 284.1736, found 284.1728. **b**: GC ($t_R$ 15.8 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.13 (hexane/EtOAc 3:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.24–1.86 (m, 12H), 2.92–3.23 (m, 2H), 3.64 (s, 6H), 3.84–4.12 (m, 2H), 4.44–4.80 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 18.9 and 19.0, 25.1 and 25.2 and 25.4, 25.8 and 25.9 and 26.3, 39.1 and 39.4 and 39.6 and 39.8, 48.1 and 48.2 and 48.6 and 48.7, 52.4 and 52.5, 156.2 and 156.4; IR (neat) 1700, 1455, 1260 cm$^{-1}$; LRMS (EI) *m/e* 284 ($M^+$), 142 ($M^+ - C_7H_{12}NO_2$); HRMS (EI) calcd for $C_{14}H_{24}N_2O_4$ 284.1736, found 284.1730.

***N,N′*-Diethyl-*N,N′*-bis(methoxycarbonyl)-2,3-butanediamine (15).** Prepared from the cation pool generated from methyl diethylcarbamate (**13**) (54.5 mg, 0.415 mmol), and purified by flash chromatography (hexane/EtOAc 5:1) (36.6 mg, 68%). This compound was characterized as a mixture of two diastereomers (48:52 by GC): GC ($t_R$ 10.4 and 11.0 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.25 (hexane/EtOAc 3:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.02–1.25 (m, 12H), 2.96–3.40 (m, 4H), 3.66 (s) and 3.70 (s) (total 6H), 3.90–4.41 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.3 and 14.6 and 15.0 and 15.1, 15.7 and 16.2 and 16.9 and 17.4, 36.9 and 38.6, 52.0 and 52.2, 53.5, 156.0 and 156.3 and 156.6 and 156.9; IR (neat) 1700, 1456, 1271 cm$^{-1}$; LRMS (EI) *m/e* 260 ($M^+$), 130 ($M^+ - C_6H_{12}NO_2$); HRMS (EI) calcd for $C_{12}H_{24}N_2O_4$ 260.1736, found 260.1732.

***N,N′*-Dibutyl-*N,N′*-bis(methoxycarbonyl)-1,2-ethanediamine (16).** Prepared from cation pool **7** (8.0 mL, 0.426 mmol) and purified by flash chromatography (hexane/EtOAc 10:1 to 5:1) (24.0 mg, 39%). TLC $R_f$ 0.27 (hexane/EtOAc 3:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.91 (t, $J = 7.2$ Hz, 6H), 1.17–1.40 (m, 4H), 1.40–1.59 (m, 4H), 3.15–3.43 (m, 8H), 3.67 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 13.9, 20.0, 30.4 and 30.9, 45.0 and 45.6 and 45.7 and 46.3, 47.8 and 48.0, 52.5, 156.6 and 156.7; IR (neat) 2959, 1699, 1480, 1229 cm$^{-1}$; LRMS (FAB) *m/e* 289 ($MH^+$), 257 ($M^+$ − OMe), 158 ($M^+ - C_6H_{12}NO_2$); HRMS (FAB) calcd for $C_{14}H_{29}N_2O_4$ ($MH^+$) 289.2127, found 289.2122.

**Methyl 2-[(*N*-Butyl-*N*-methoxycarbonyl)aminomethyl]pyrrolidine-1-carboxylate (18).** Prepared from mixture of cation pools **2** (3.2 mL, 0.171 mmol) and **7** (3.2 mL, 0.160 mmol) and purified by flash chromatography (hexane/EtOAc 10:1 to 5:1) (11.1 mg, 0.0409 mmol): TLC $R_f$ 0.25 (hexane/EtOAc 3:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.91 (t, $J = 7.2$ Hz, 3H), 1.16–1.37 (m, 2H), 1.37–1.62 (m, 2H), 1.62–2.05 (m, 4H), 3.01–3.52 (m, 6H) 3.68 (s, 6H), 3.96–4.07 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 13.9, 20.1, 22.8 and 23.7, 28.1 and 28.8, 30.1 and 30.7, 46.4 and 46.6, 46.9 and 47.2, 47.7 and 48.1, 49.0 and 49.3, 52.3 and 52.5, 55.8 and 56.6, 155.5, 156.6 and 157.6; IR (neat) 2957, 1700, 1456, 1385 cm$^{-1}$; LRMS (FAB) *m/e* 273 ($MH^+$), 241 ($M^+$ − OMe), 128 ($M^+ - C_7H_{14}NO_2$); HRMS (FAB) calcd for $C_{13}H_{25}N_2O_4$ ($MH^+$) 273.1814, found 273.1813.

**Methyl 2-[2-(Methoxycarbonyl)ethyl]pyrrolidine-1-carboxylate (19). Typical Procedure of Reductive Coupling of Cation Pool and Activated Olefin:** Electrochemical reductive coupling was carried out in an H-type divided cell (4G glass filter) having two chambers: chamber A equipped with a carbon-felt electrode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 °C/1 mmHg for 2 h before use); chamber B equipped with a platinium plate electrode (30 mm × 25 mm) and a carbon-rod electrode (Touhou Tanso Kougyou ER-38H, diameter 7 mm). In chamber A were placed **1** (51.4 mg, 0.398 mmol) and 0.06 M $Bu_4NBF_4/CH_2Cl_2$ (40.0 mL). In chamber B were placed trifluoromethanesulfonic acid (143.8 mg, 0.958 mmol) and 0.06 M $Bu_4NBF_4/CH_2Cl_2$ (40.0 mL). Constant-current electrolysis (8 mA) was carried out by using the carbon-felt electrode in chamber A as an anode and the platinum-plate electrode in chamber B as a cathode at −78 °C with stirring until 2.5 F/mol of electricity was consumed. Thus, the cation pool of **2** was genarated. After the anodic oxidation of **1** was completed, methyl acrylate (171.5 mg, 1.99 mmol) and trifluoromethanesulfonic acid (3.124 g, 20.8 mmol) were added to the solution in chamber A. To the solution in chamber B was added THF (261.3 mg, 3.62 mmol), which would serve as a substrate for oxidation during the reduction of **2** in chamber A. Constant-current electrolysis (8 mA) was carried out using the carbon felt electrode in chamber A as a cathode and the carbon-rod electrode in chamber B as an anode at −78 °C with stirring until 2.5 F/mol of electricity was consumed. $Et_3N$ (2.157 g, 21.3 mmol) was added to the solution in chamber A to neutralize the reaction mixture and the mixture was warmed to room temperature. The reaction mixture in the chamber A was transferred to a flask and the solvent was removed

under reduced pressure. 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 (300 mL). The GC analysis of the combined filtrate indicated that **6** was produced in 88% yield. The crude product was purified by flash chromatography (hexane/EtOAc 7:1 to 5:1): GC ($t_R$ 8.2 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.45 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.60–2.12 (m, 6H), 2.25–2.43 (m, 2H), 3.27–3.56 (m, 2H), 3.68 (s, 3H), 3.68 (s, 3H), 3.79–3.94 (m, 1H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 22.6 and 23.4, 29.1 and 29.3, 29.7, 30.4 and 30.7, 45.9 and 46.2, 51.1, 51.8, 56.0 and 56.8, 155.4, 173.3 and 173.4; IR (neat) 1748, 1700, 1385 cm$^{-1}$; LRMS (EI) $m/e$ 215 ($M^+$), 128 ($M^+ - C_4H_7O_2$); HRMS (EI) calcd for $C_{10}H_{17}NO_4$ 215.1158, found 215.1159; Anal. Calcd for $C_{10}H_{17}NO_4$: C, 55.80; H, 7.96; N, 6.51%. Found: C, 55.67; H, 8.10; N, 6.29%.

**Methyl 1,2-Bis(*N*-carbomethoxypyrrolidin-2-yl)propanoate (22).** This compound was obtained as a by-product in the reductive coupling of the cation pool **2** and methyl acrylate. Purified by flash chromatography (hexane/EtOAc 1:1 to 1:2) and GPC: TLC $R_f$ 0.23 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.37–2.21 (m, 9H), 2.21–2.46 (m, 2H), 3.20–3.55 (m, 4H), 3.65 (s, 3H), 3.65 (s, 3H), 3.70 (s, 3H), 3.81–4.23 (m, 2H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 22.6 and 22.8 and 22.9 and 23.1, 23.4 and 23.5 and 23.7 and 27.9 and 28.1, 29.4 and 29.7, 30.4 and 30.6 and 30.8 and 31.1, 32.7 and 33.3 and 33.5 and 33.6 and 34.0, 43.1 and 43.4 and 44.0 and 44.3 and 44.5 and 44.6 and 45.1, 46.0 and 46.2 and 46.4, 46.9 and 47.4, 51.5, 51.9 and 52.0, 52.1 and 52.3, 55.4 and 55.6 and 55.9 and 56.2, 58.2 and 58.8 and 59.0 and 59.2 and 60.1, 155.3, 155.4, 173.8 and 174.3; IR (neat) 1732, 1700, 1387 cm$^{-1}$; LRMS (EI) $m/e$ 342 ($M^+$), 128 ($M^+ - C_{10}H_{16}NO_4$); HRMS (EI) calcd for $C_{16}H_{26}N_2O_6$ 342.1791, found 342.1785; Anal. Calcd for $C_{16}H_{26}N_2O_6$: C, 56.13; H, 7.65; N, 8.18%. Found: C, 55.95; H, 7.67; N, 7.92%.

**Methyl 2-[2-(Isobutoxycarbonyl)ethyl]pyrrolidine-1-carboxylate.** Prepared from the cation pool that was generated from **1** (51.5 mg, 0.399 mmol) and isobutyl acrylate (407.5 mg, 3.18 mmol), and purified by flash chromatography (hexane/EtOAc 7:1) (77.3 mg, 75%): TLC $R_f$ 0.65 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.91 (d, $J = 6.6$ Hz, 6H), 1.57–1.76 (m, 2H), 1.76–2.06 (m, 5H), 2.24–2.39 (m, 2H), 3.25–3.53 (m, 2H), 3.66 (s, 3H), 3.77–3.93 (m, 1H), 3.83 (d, $J = 6.6$ Hz, 2H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 19.0, 22.9 and 23.7, 27.6, 29.4 and 29.6, 29.9 and 30.6, 31.0 and 31.2, 46.1 and 46.5, 52.1, 56.4 and 57.1, 70.5, 155.7, 173.3 and 173.4; IR (neat) 1734, 1700 1385 cm$^{-1}$; LRMS (EI) $m/e$ 257 ($M^+$), 128 ($M^+ - C_7H_{13}O_2$); HRMS (EI) calcd for $C_{13}H_{23}NO_4$ 257.1627, found 257.1633.

**Methyl 2-[2-(Methoxycarbonyl)propyl]pyrrolidine-1-carboxylate.** Prepared from the cation pool that was generated from **1** (51.4 mg, 0.398 mmol) and methyl methacrylate (314.3 mg, 3.14 mmol), and purified by flash chromatography (hexane/EtOAc 7:1) (70.7 mg, 77%). This compound was characterized as a mixture of two diastereomers (59:41 by GC): GC ($t_R$ 8.3 and 8.5 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.52 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.08–1.43 (m, 3H), 1.51–1.68 (m, 1H), 1.68–1.97 (m, 4H), 1.97–2.22 (m, 1H), 2.38–2.63 (m, 1H), 3.24–3.50 (m, 2H), 3.65 (s, 3H), 3.66 (s, 3H), 3.76–4.02 (m, 1H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 17.6, 22.8 and 23.7, 29.9 and 30.5 and 30.9, 36.6 and 37.8 and 38.4 and 38.6 and 38.8, 36.9, 46.0 and 46.3, 51.5, 52.0 and 52.1, 55.2 and 55.6 and 56.2, 155.6, 176.8; IR (neat) 1730, 1700, 1387 cm$^{-1}$; LRMS (EI) $m/e$ 229 ($M^+$), 142 ($M^+ - C_4H_7O_2$), 128 ($M^+ - C_5H_9O_2$); HRMS (EI) calcd for $C_{11}H_{19}NO_4$ 229.1314, found 229.1307; Anal. Calcd for $C_{11}H_{19}NO_4$: C, 57.62; H, 8.35; N, 6.11%. Found: C, 57.53; H, 8.11; N, 6.01%.

**Methyl 2-(2-Methoxycarbonyl-1-methylethyl)pyrrolidine-1-carboxylate.** Prepared from the cation pool that was generated from **1** (52.9 mg, 0.410 mmol) and methyl crotonate (792.4 mg, 7.91 mmol), and purified by flash chromatography (hexane/EtOAc 7:1) (29.9 mg, 32%). This compound was characterized as a mixture of two diastereomers (64:36 by GC): GC ($t_R$ 8.5 and 8.7 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.52 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.78–0.94 (m, 3H), 1.56–1.98 (m, 4H), 1.98–2.17 (m, 1H), 2.24–2.70 (m, 2H), 3.14–3.27 (m, 1H), 3.27–3.46 (m, 1H), 3.64 (s, 3H), 3.68 (s, 3H), 3.72–3.90 (m, 1H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 15.6 and 15.9 and 16.7, 23.2 and 23.6 and 23.9 and 24.3, 26.3 and 27.2 and 27.6, 32.8 and 33.2 and 36.4 and 36.7, 33.6 and 38.5, 46.4 and 46.9 and 47.1 and 47.6, 51.4, 52.2, 60.9 and 61.2 and 61.7 and 61.9, 156.0, 173.4 and 173.5; IR (neat) 1738, 1699, 1379 cm$^{-1}$; LRMS (EI) $m/e$ 229 ($M^+$), 128 ($M^+ - C_5H_9O_2$); HRMS (EI) calcd for $C_{11}H_{19}NO_4$ 229.1314, found 229.1316; Anal. Calcd for $C_{11}H_{19}NO_4$: C, 57.62; H, 8.35; N, 6.11%. Found: C, 57.75; H, 8.06; N, 5.88%.

**Methyl 2-[1,2-Bis(methoxycarbonyl)ethyl]pyrrolidine-1-carboxylate.** Prepared from the cation pool that was generated from **1** (51.0 mg, 0.395 mmol) and dimethyl fumarate (455.7 mg, 3.16 mmol), and purified by flash chromatography (hexane/EtOAc 3:1) (41.8 mg, 39%). This compound was characterized as a mixture of two diastereomers (53:47 by GC): GC ($t_R$ 13.4 and 13.6 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.44 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.63–2.00 (m, 4H), 2.24–2.53 (m, 1H), 2.64–2.82 (m, 1H), 3.08–3.32 (m, 1H), 3.32–3.78 (m, 2H), 3.62 (s, 3H), 3.66 (s, 3H), 3.66 (s, 3H), 4.02–4.30 (m, 1H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 22.7 and 23.5 and 24.1, 27.2 and 28.1 and 29.2, 30.5 and 30.9 and 33.0 and 33.4, 42.2 and 43.5 and 44.2 and 44.5, 46.3 and 46.8 and 47.0 and 47.6, 51.7, 52.0, 52.4, 57.2 and 57.6 and 58.2 and 58.8, 155.6, 172.2, 173.5; IR (neat) 1737, 1700, 1383 cm$^{-1}$; LRMS (EI) $m/e$ 273 ($M^+$), 200 ($M^+ - C_3H_5O_2$), 128 ($M^+ - C_6H_9O_4$); HRMS (EI) calcd for $C_{12}H_{19}NO_6$ 273.1212, found 273.1206.

**Methyl 2-(2-Oxooxolane-2-ylmethyl)pyrrolidine-1-carboxylate.** Prepared from the cation pool that was generated from **1** (51.8 mg, 0.401 mmol) and $\alpha$-methylene-$\gamma$-butyrolactone (196.8 mg, 2.01 mmol), and purified by flash chromatography (hexane/EtOAc 3:1) (65.0 mg, 71%). This compound was characterized as a mixture of two diastereomers (73:27 by GC): GC ($t_R$ 14.2 and 14.3 min, column, OV-1; 0.25 mm × 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min); TLC $R_f$ 0.23 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.32–1.77 (m, 2H), 1.77–2.27 (m, 5H), 2.34–2.88 (m, 2H), 3.20–3.57 (m, 2H), 3.64 (s, 3H), 3.76–4.11 (m, 1H), 4.11–4.25 (m, 1H), 4.25–4.41 (m, 1H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 22.6 and 22.8 and 23.5, 28.5 and 31.1, 29.3 and 29.5, 35.1 and 36.6, 35.6 and 37.3, 46.0 and 46.4, 52.2, 55.2 and 55.5 and 56.3, 66.4 and 66.6, 155.5 and 155.7 and 156.5, 179.1 and 179.2 and 179.7; IR (neat) 1770, 1695, 1385 cm$^{-1}$; LRMS (EI) $m/e$ 227 ($M^+$), 196 ($M^+ - OCH_3$), 128 ($M^+ - C_5H_7O_2$); HRMS (EI) calcd for $C_{11}H_{17}NO_4$ 227.1158, found 227.1160.

**Methyl 2-[2-(Methoxycarbonyl)ethyl]piperidine-1-carbox-**

**ylate.** Prepared from the cation pool that was generated from *N*-(methoxycarbonyl)piperidine (51.8, 0.362 mmol) and methyl acrylate (151.2 mg, 1.756 mmol), and purified by flash chromatography (hexane/EtOAc 10:1) (45.4 mg, 53%): TLC $R_f$ 0.39 (hexane/EtOAc 3:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.28–1.47 (m, 1H), 1.50–1.76 (m, 6H), 2.02–2.21 (m, 1H), 2.23–2.35 (m, 2H), 2.72–2.87 (m, 1H), 3.66 (s, 3H), 3.66 (s, 3H), 3.84–4.12 (m, 1H), 4.12–4.41 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 18.9, 24.8, 25.4, 28.7, 30.8, 38.8, 50.1, 51.5, 52.4, 156.1, 173.8; IR (neat) 1741, 1700, 1444 cm$^{-1}$; LRMS (EI) *m*/*e* 229 ($M^+$), 170 ($M^+ - C_2H_3O_2$), 142 ($M^+ - C_4H_7O_2$); HRMS (EI) calcd for $C_{11}H_{19}NO_4$ 229.1314, found 229.1318.

**Methyl 4-[(*N*-Ethyl-*N*-methoxycarbonyl)amino]pentanoate.** Prepared from the cation pool that was generated from *N*-(methoxycarbonyl)diethylamine (53.2 mg, 0.406 mmol) and methyl acrylate (181.5 mg, 2.11 mmol), and purified by flash chromatography (hexane/EtOAc 10:1) (56.0 mg, 63%): TLC $R_f$ 0.33 (hexane/EtOAc 3:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.07–1.21 (m, 3H), 1.17 (d, $J = 6.9$ Hz, 3H), 1.68–1.92 (m, 2H), 2.28 (t, $J = 7.4$ Hz, 2H), 2.96–3.39 (m, 2H), 3.66 (s, 3H), 3.68 (s, 3H), 3.87–4.25 (m, 1H); $^{13}$C NMR (125.65 MHz, $CDCl_3$) $\delta$ 14.7 and 15.4, 19.0 and 19.5, 29.5, 31.1, 37.3 and 37.9, 51.2, 51.4, 52.1, 156.4 and 156.8, 173.6; IR (neat) 1736, 1700, 1439 cm$^{-1}$; LRMS (EI) *m*/*e* 217 ($M^+$), 158 ($M^+ - C_2H_3O_2$), 130 ($M^+ - C_4H_7O_2$); HRMS (EI) calcd for $C_{10}H_{19}NO_4$ 217.1314, found 217.1317.

**Methyl 2-(2-Cyanoethyl)pyrrolidine-1-carboxylate.** Prepared from cation pool **2** (8.0 mL, 0.390 mmol) and acrylonitrile (107.0 mg, 2.017 mmol), and purified by flash chromatography (hexane/EtOAc 2:1) (8.6 mg, 12%). TLC $R_f$ 0.33 (hexane/EtOAc 1:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.54–2.11 (m, 6H), 2.29–2.47 (m, 2H), 3.27–3.58 (m, 2H), 3.69 (s, 3H), 3.87–3.99 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 14.6, 23.2 and 23.9, 30.5 and 30.9, 30.7, 46.6, 52.5, 56.9, 119.6, 155.5; IR (neat) 2957, 1696, 1456, 1385 cm$^{-1}$; LRMS (EI) *m*/*e* 182 ($M^+$), 128 ($M^+ - C_3H_4N$); HRMS (EI) calcd for $C_9H_{14}N_2O_2$ 182.1055, found 182.1054.

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