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Electrochemical carboxylation of bicyclo[*n*.1.0]alkylidene derivatives

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Abstract—Electrochemical carboxylation of bicyclo[*n*.1.0]alkylidene derivatives (ring-fused alkylidenecyclopropanes) in a suitable aprotic solvent using a one-compartment electrochemical cell equipped with a platinum plate cathode and a zinc plate anode under an atmospheric pressure of carbon dioxide afforded either mono- or dicarboxylic acid in moderate to good yields.

1. Introduction

Electrochemical carboxylation is one of the most useful methods for the fixation of carbon dioxide to organic molecules because it is a clean and environmentally benign process. It takes place efficiently even in an atmospheric pressure of CO_2 under neutral and mild conditions to give carboxylic acids in high yields when a reactive-metal such as magnesium or aluminum is used as a sacrificial anode in the electrolysis.[1–4] Carbon dioxide is non-toxic and can work as an electrophile in the reaction of anion species to give carboxylic acids with one carbon elongation. We have already reported that electrochemical fixation of carbon dioxide to various organic molecules such as allylic halides,[5] propargylic bromide,[6] 2-bromomethyl-1,4-dibromobut-2-ene,[7] vinyl bromides,[8] and vinyl triflates[9] proceeded efficiently, regio- and chemoselectively to give the corresponding carboxylic acids in high yields. We have also reported an efficient synthesis of 2-phenylsuccinic acid derivatives by electrochemical dicarboxylation of phenyl substituted alkenes.[10] In addition, it has been reported by several researchers that electrochemical carboxylation of activated olefins having electron-withdrawing groups gave mono- or dicarboxylic acids.[11] However, only simple activated olefins such as methyl vinyl ketone, acrylonitrile, and methyl acrylate were used in these electrochemical carboxylation as substrates. To the best of our knowledge, there has been no report of the electrochemical carboxylation reactions of alkylidenecyclopropane derivatives. Methylene- and alkylidenecyclopropanes are very attractive substrates in organic reactions due to their unique reactivities originating from their highly strain structures. They have been widely used for many kind of organic reactions; i.e., cycloaddition reactions,[12,13] photochemical reactions,[14] and transition-metal catalyzed reactions.[15–20] Besides alkylidenecyclopropanes are widely used for the syntheses of various heterocycles which have been summarized in a review.[21] Recently we reported a facile method for the preparation of alkylidenecyclopropane derivatives carrying activated olefin unit[22] and its transformation to alkylidenecyclobutanes.[23] As an extension of our studies on electrochemical carboxylations, we recently carried out the electrochemical carboxylation of bicyclo[*n*.1.0]alkylidene derivatives (ring-fused alkylidenecyclopropanes), and wish to report here the results. By electrolysis of a system containing both carbon dioxide and ring-fused alkylidenecyclopropane derivatives **1** or **4** in one-compartment electrochemical cell using a platinum plate cathode and a zinc plate anode under atmospheric pressure in a suitable aprotic solvent such as DMF or MeCN, it is possible to achieve either a direct synthesis of monocarboxylic acid **2** or **5**/or dicarboxylic acid **3** or **6** (Scheme 1).

2. Results and discussion

Electrochemical carboxylation of bicyclo[4.1.0]hept-7-ylidene derivatives **1** was carried out in a dry DMF solution containing tetraethylammonium perchlorate (TEAP) as a supporting electrolyte under a slow stream of carbon dioxide gas in a one-compartment electrochemical cell equipped with a platinum plate cathode (2×3 cm^2) and a zinc plate anode (2×3 cm^2) (Scheme 2). The results are summarized in Table 1. In all cases, compounds **1** were

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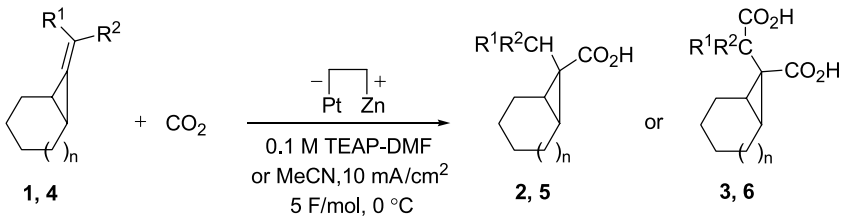
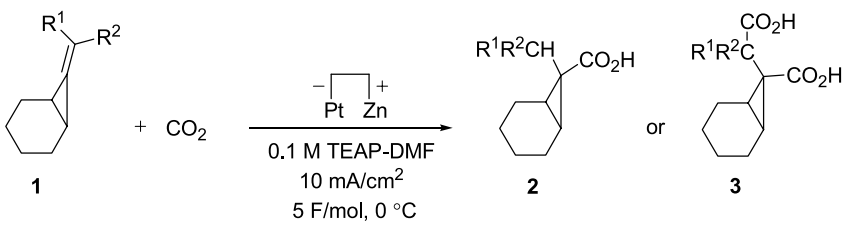


1-3 (n=1) 4-6 (n=2)	R^1	R^2
a	H	COOMe
b	H	COOEt
c	H	COMe
d	Me	COOMe
e	$CH_2CH=CH_2$	COOMe

Scheme 1.



Scheme 2.

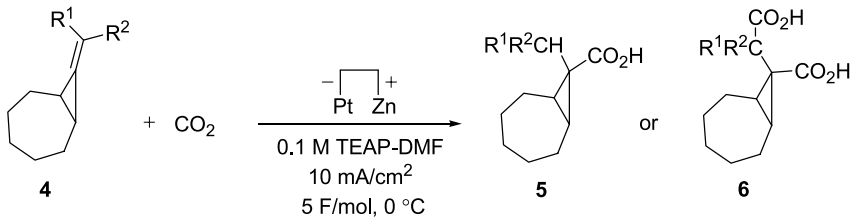
Table 1. Electrochemical carboxylation of bicyclo[4.1.0]hept-7-ylidene derivatives **1** in DMF[a]

R^1	R^2	Product	Yield (%)[b]
H	COOMe (**1a**)	**2a**	44
H	COOEt (**1b**)	**3b**	48
H	COMe (**1c**)	**2c**	61
Me	COOMe (**1d**)	**2d**	47
$CH_2CH=CH_2$	COOMe (**1e**)	**2e**	74

[a] **1** (2 mmol), Et_4NClO_4 (2 mmol), DMF (20 mL) in a one-compartment electrochemical cell.
[b] Isolated yields.

carboxylated under a constant current until 5 F/mol of charge with a current density of 10 mA/cm^2 had passed through the cell at 0 °C.

Electrochemical carboxylation of **1c** and **1e** took place efficiently to give the corresponding monocarboxylic acids **2c** and **2e** in isolated yields of 61 and 74%, respectively. On the other hand, electrochemical carboxylation of **1a** and **1d** occurred less effectively to give **2a** and **2d** in the yield of 44 and 47%, respectively. However, similar electrochemical carboxylation of **1b** under the same conditions gave no



Scheme 3.

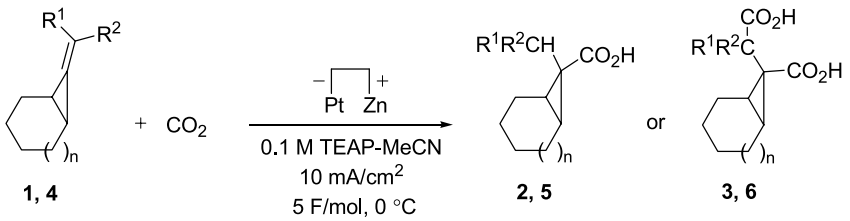
Table 2. Electrochemical carboxylation of bicyclo[5.1.0]oct-8-ylidene derivatives **4** in DMF[a]

R^1	R^2	Product	Yield (%)[b]
H	COOMe (**4a**)	**6a**	34
H	COOEt (**4b**)	**6b**	48
Me	COOMe (**4d**)	**5d**	65
$CH_2CH=CH_2$	COOMe (**4e**)	**5e**	68

[a] **4** (2 mmol), Et_4NClO_4 (2 mmol), DMF (20 mL) in a one-compartment electrochemical cell.
[b] Isolated yields.

monocarboxylic acid and, instead, dicarboxylic acid **3b** was obtained in 48% yield.

Electrochemical carboxylation of bicyclo[5.1.0]oct-8-ylidene derivatives **4** was carried out under the same conditions as those applied for bicyclo[4.1.0]hept-7-ylidene derivatives (Scheme 3). The results are summarized in Table 2. Carboxylation of **4a** and **4b** afforded dicarboxylic acids **6a** and **6b** in 34 and 48% isolated yields, respectively. On the other hand, **4d** and **4e** afforded no dicarboxylic acids and, instead, monocarboxylic acids **5d** and **5e** were



Scheme 4.

Table 3. Electrochemical carboxylation of bicyclo[*n*.1.0]alkylidene derivatives **1** and **4** in MeCN[a]

n	R^1	R^2	Product	Yield (%)[b]
1	H	COOEt (**1b**)	**3b**	71
1	Me	COOMe (**1d**)	**2d**	24
2	H	COOMe (**4a**)	**6a**	66
2	H	COOEt (**4b**)	**6b**	75

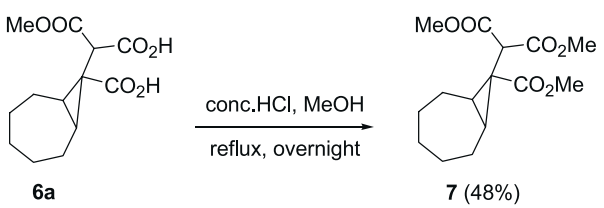
[a] **1** or **4** (2 mmol), Et_4NClO_4 (2 mmol), MeCN (20 mL) in a one-compartment electrochemical cell.
[b] Isolated yields.

obtained exclusively in the yield of 65 and 68%, respectively.

Some electrochemical carboxylation reactions of **1** and **4** were carried out in dry MeCN to investigate whether the yields increase or not. The carboxylation was carried out in a dry MeCN solution containing TEAP as a supporting electrolyte in a one-compartment electrochemical cell equipped with a platinum plate cathode (2×3 cm^2) and a zinc plate anode (2×3 cm^2) (Scheme 4). In all cases, compounds **1** and **4** were carboxylated under a slow stream of carbon dioxide gas at a constant current of 10 mA/cm^2 until 5 F/mol of charge had passed through the cell at 0 °C. The results are summarized in Table 3.

The electrochemical carboxylation of **1b**, **4a** and **4b** in MeCN took place more efficiently to give the dicarboxylic acids **3b**, **6a** and **6b** in 71, 66 and 75% isolated yields, respectively, whereas in DMF these were 48, 34 and 48%, respectively. On the other hand, electrochemical carboxylation of **1d** in MeCN under the same conditions took place less efficiently and afforded monocarboxylic acid **2d** in 24% isolated yield whereas in DMF it gave the same product **2d** in 47% yield. It is not clear the reasons in this moment why monocarboxylation is better in DMF and dicarboxylation is better in MeCN regardless the bicyclic systems of the ring-fused alkylidenecyclopropanes.

The structures of dicarboxylic acids **3** or **6** were determined by those spectral data and the following results. When the dicarboxylic acid **6a** containing a methyl ester group was refluxed with concentrated hydrochloric acid in methanol



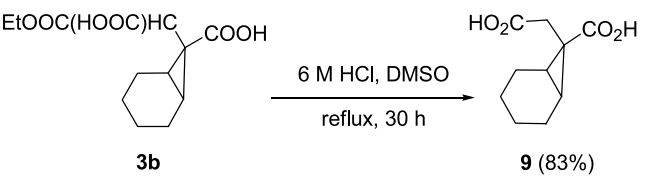
Scheme 5.

for overnight, trimethyl ester **7** was obtained in the yield of 48% (Scheme 5). ^1H NMR spectra of **7** showed two peaks of methoxy groups with different chemical shifts at δ 3.65 (s, 3H) and at δ 3.77 (s, 6H) indicating the presence of two carboxyl groups in **6a** which were esterified to methyl esters.

Stirring of **6a** with 6 M hydrochloric acid in DMSO under reflux for 30 h, decarboxylation of one carboxylic group took place along with the conversion of methyl ester to acid and afforded **8** in 94% yield (Scheme 6). It also indicates the presence of two carboxyl groups in **6a**.

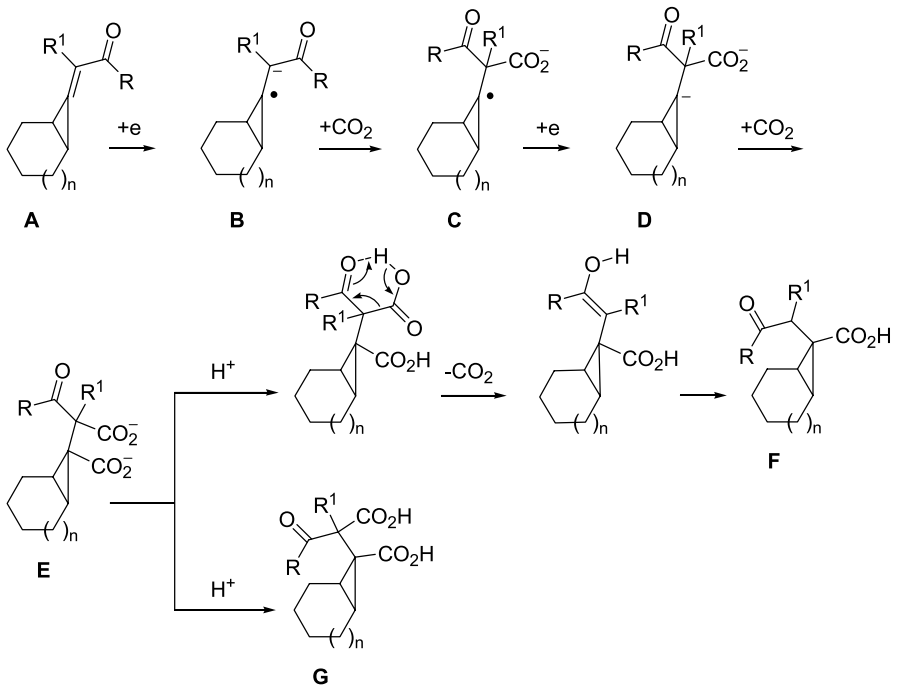
Scheme 6.

The *endo*- or *exo*-configuration of the mono- and dicarboxylic acids **2**, **3** and **5**, **6** was established by comparing the spectral data of its derivatives with those reported in the literature.[24] Stirring of **3b** with 6 M hydrochloric acid in DMSO under reflux for 30 h afforded **9** in 83% yield (Scheme 7). The melting point and spectral data of **9** supported the 7-*endo*-substituted-7-*exo*-carboxylic acid configuration of **3b**.[24] Usually, activated ring-fused alkylidenecyclopropanes favour nucleophilic attack from *exo*-direction.[25]



Scheme 7.

The electrochemical carboxylation of olefinic substrates with CO_2 in aprotic solvents has already been proposed as a useful procedure for the production of mono- and dicarboxylic acids.[11] Proposed reaction pathways of the present electrochemical carboxylations are shown in Scheme 8. Activated olefins **A** are easier to be reduced than CO_2, since reduction potential of bicyclo[*n*.1.0]alkylidene derivatives **1a**–**1e**, **4a**–**4e** and CO_2 are −2.35–−2.71 V, −2.56–−2.71 V and −2.90 V vs Ag/Ag^+, respectively.[26] Therefore, a one-electron reduction of activated olefins **A** would give the anion radical **B**, which



Scheme 8.

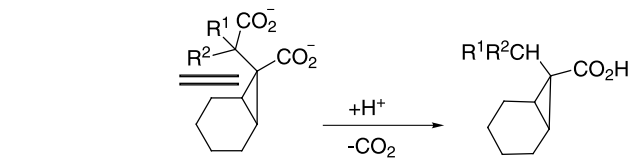


Figure 1.

undergoes a nucleophilic attack on CO_2 to give the anion radical **C**. Further one-electron reduction of **C** affords the carbanion **D**,[11a,27] which would react with another CO_2 at the *exo*-position of **D** to give dicarboxylate anion **E**. Similar pathways in the electrochemical reduction of α,β-unsaturated carbonyl compounds have been pointed out by Wawzonek and co-workers.[28] We assume that the present electrochemical carboxylation of both mono- and disubstituted bicyclo[*n*.1.0]alkylidene derivatives give dicarboxylate anions **E**. On acidification during work-up the dicarboxylate anions **E** of all mono (except **1b**) and disubstituted bicyclo[4.1.0]hept-7-ylidene derivatives **1a**, **1c–e** and disubstituted bicyclo[5.1.0]oct-8-ylidene derivatives **4d–e** gave monocarboxylic acids **F** via decarboxylation of one carboxyl group bearing carbonyl group at the α-position. On the other hand, in the case of monosubstituted bicyclo[5.1.0]oct-8-ylidene derivatives **4a–b**, acidification of **E** gave dicarboxylic acids **G** (Scheme 8).

Dicarboxylated bicyclo[4.1.0]heptane derivatives are spatially more rigid, greater ring-strain and sterically more hindered. Therefore, decarboxylation of one carboxyl group can release the strain and afforded monocarboxylic acids (Fig. 1). It is not clear at the present stage that no

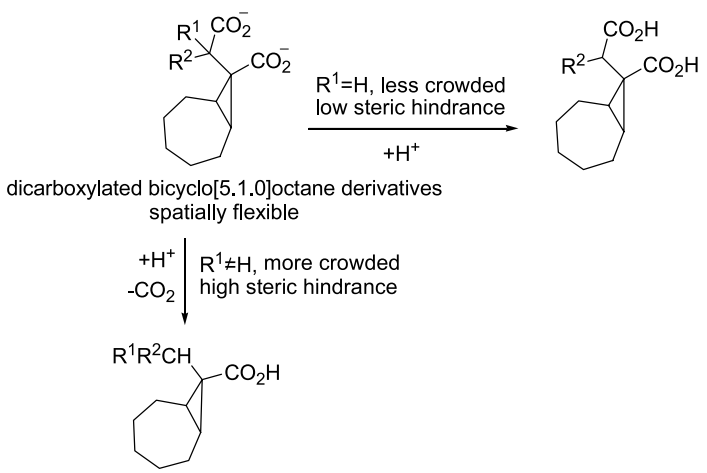


Figure 2.

decarboxylation occurred to give dicarboxylic acid **3b** only in the case of bicyclo[4.1.0]hept-7-ylideneacetic acid ethyl ester (**1b**).

On the other hand, dicarboxylated bicyclo[5.1.0]octane derivatives are spatially flexible and sterically less hindered when R^1=H but more hindered when R^1≠H. As a result, decarboxylation of one carboxylic group minimizes the steric hindrance and afforded monocarboxylic acids when R^1≠H. However, when R^1=H no such steric hindrance prevails and afforded dicarboxylic acids (Fig. 2).

3. Experimental

3.1. General

Melting points were uncorrected and measured with a Yanagimoto micro mp apparatus. IR spectra were determined for nujol mulls, unless otherwise noted, with a JASCO IR-810 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 270 MHz and 67.5 MHz, respectively, with a JEOL JNM EX-270 high-resolution spectrometer using $CDCl_3$ as a solvent. Chemical shifts are given in ppm down field (δ) from TMS as an internal standard. MS spectra were determined using a JEOL JMS FABmate or JMS HX-110. Cyclic voltammetries were measured with a BAS CV-50W voltammetry analyzer using a gold disk electrode (1.6 mmϕ) and Ag:$AgNO_3$ as a reference electrode. Bicyclo[*n*.1.0]alkylidene derivatives (ring-fused alkylidenecyclopropanes) were prepared according to our reported method.[22]

3.2. General procedure for electrochemical carboxylation of bicyclo[*n*.1.0]alkylidene derivatives 1 and 4

A mixture of **1** or **4** (2 mmol) and TEAP (2 mmol) in dry DMF or MeCN (20 mL) was taken into a one-compartment electrochemical cell equipped with a platinum plate cathode (2×3 cm^2) and a zinc plate anode (2×3 cm^2). The solution was electrolyzed at a constant current of 10 mA/cm^2 under a slow stream of carbon dioxide gas until electricity of 5 F/mol of substrate was passed at 0 °C. The electrolyzed solution was acidified with 2 N HCl and extracted with diethyl ether (3×25 mL). The combined ether extracts were washed successively with water (2×25 mL) and saturated aqueous sodium hydrogen carbonate (75 mL). The aqueous layer was washed with diethyl ether (2×20 mL) and again acidified with 2 N HCl and extracted with diethyl ether (3×25 mL). The combined ether extracts were washed with brine (25 mL) and dried over $MgSO_4$. Evaporation of the solvents in vacuo afforded either monocarboxylic acid **2** or **5**, or dicarboxylic acid **3** or **6**. Analytical samples were obtained by recrystallization.

3.2.1. 7-Methoxycarbonylmethylbicyclo[4.1.0]heptane-7-carboxylic acid (2a). Electrochemical carboxylation of bicyclo[4.1.0]hept-7-ylideneacetic acid methyl ester (**1a**) (332 mg, 2 mmol) in DMF gave 7-methoxycarbonylmethylbicyclo[4.1.0]heptane-7-carboxylic acid (**2a**) (188 mg, 44%): mp 136–138 °C (pet. ether); IR ν 3600–2000 (broad), 1742, 1674 cm^{-1}; ^{1}H NMR δ 1.05–1.55 (m, 6H), 1.75–2.15 (m, 4H), 2.65 (s, 2H), 3.70 (s, 3H); ^{13}C NMR δ 18.78, 21.51, 23.70, 27.42, 30.35, 51.83, 172.36, 181.56; FABMS *m*/*z* (relative intensity) 213 (MH$^+$, 22), 195 (35), 154 (100), 136 (83), 107 (27), 89 (28), 77 (27), 55 (15); HRMS calcd for $C_{11}H_{17}O_4$ *m*/*z* 213.1127. Found *m*/*z* 213.1136. Anal. calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.10; H, 7.59.

3.2.2. 2-(7-Carboxybicyclo[4.1.0]hept-7-yl)malonic acid monoethyl ester (3b). Electrochemical carboxylation of bicyclo[4.1.0]hept-7-ylideneacetic acid ethyl ester (**1b**) (360 mg, 2 mmol) in MeCN gave 2-(7-carboxybicyclo-[4.1.0]hept-7-yl)malonic acid monoethyl ester (**3b**) (383 mg, 71%): mp 167–169 °C (ethyl acetate); IR ν 3600–2000 (broad), 1753, 1709, 1677 cm^{-1}; ^{1}H NMR δ 1.12–1.61 (m, 6H), 1.27 (t, *J*=7.26 Hz, 3H), 1.75–2.14 (m, 4H), 3.24 (s, 1H), 4.21 (q, *J*=7.26 Hz, 2H); ^{13}C NMR δ 13.23, 18.00, 18.07, 20.61, 22.12, 22.41, 30.33, 48.22, 60.19, 168.29, 169.33, 175.09; FABMS *m*/*z* (relative intensity) 271 (MH$^+$, 34), 253 (79), 154 (100), 136 (91), 107 (32), 89 (32), 77 (32), 55 (19); HRMS calcd for $C_{13}H_{19}O_6$ *m*/*z* 271.1182. Found *m*/*z* 271.1154. Anal. calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.68; H, 6.69.

3.2.3. 7-(2-Oxopropyl)bicyclo[4.1.0]heptane-7-carboxylic acid (2c). Electrochemical carboxylation of bicyclo[4.1.0]hept-7-ylidenepropan-2-one (**1c**) (300 mg, 2 mmol) in DMF gave 7-(2-oxopropyl)bicyclo[4.1.0]heptane-7-carboxylic acid (**2c**) (239 mg, 61%): mp 96–97 °C (pet. ether); IR ν 3600–2000 (broad), 3322, 1727 cm^{-1}; ^{1}H NMR δ 1.05–1.50 (m, 6H), 1.65–2.10 (m, 4H), 1.73 (bs, 3H), 2.45 (bs, 2H); ^{13}C NMR δ 19.43, 21.60, 23.04, 28.30, 29.29, 180.70; EIMS *m*/*z* (relative intensity) 196 (M$^+$, 10), 178 (31), 153 (57), 135 (73), 107 (88), 93 (35), 79 (57); HRMS calcd for $C_{11}H_{16}O_3$ *m*/*z* 196.1099. Found *m*/*z* 196.1100. Anal. calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.03; H, 8.18.

3.2.4. 7-(1-Methoxycarbonylethyl)bicyclo[4.1.0]heptane-7-carboxylic acid (2d). Electrochemical carboxylation of 2-bicyclo[4.1.0]hept-7-ylidenepropanoic acid methyl ester (**1d**) (360 mg, 2 mmol) in DMF gave 7-(1-methoxycarbonylethyl)bicyclo[4.1.0]heptane-7-carboxylic acid (**2d**) (213 mg, 47%): mp 145–147 °C (ethyl acetate); IR ν 3600–2000 (broad), 1737, 1679 cm^{-1}; ^{1}H NMR δ 1.12–1.55 (m, 6H), 1.41 (d, *J*=6.93 Hz, 3H), 1.55–2.15 (m, 4H), 2.34 (q, *J*=6.93 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR δ 14.04, 19.03, 19.23, 21.57, 21.82, 23.74, 25.84, 33.39, 35.94, 51.97, 175.09, 180.72; EIMS *m*/*z* (relative intensity) 226 (M$^+$, 2), 208 (24), 195 (12), 180 (100), 166 (37), 148 (61), 121 (80), 93 (72), 79 (56), 67 (42), 55 (27); HRMS calcd for $C_{12}H_{18}O_4$ *m*/*z* 226.1205. Found *m*/*z* 226.1183. Anal. calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.91; H, 8.07.

3.2.5. 7-(1-Methoxycarbonylbut-3-enyl)bicyclo[4.1.0]-heptane-7-carboxylic acid (2e). Electrochemical carboxylation of 2-bicyclo[4.1.0]hept-7-ylidenepent-4-enoic acid methyl ester (**1e**) (412 mg, 2 mmol) in DMF gave 7-(1-methoxycarbonylbut-3-enyl)bicyclo[4.1.0]heptane-7-carboxylic acid (**2e**) (373 mg, 74%): mp 100–101 °C (pet. ether); IR ν 3600–2000 (broad), 1742, 1678 cm^{-1}; ^{1}H NMR δ 1.15–1.57 (m, 6H), 1.57–2.10 (m, 4H), 2.15–2.35 (m, 2H), 2.95–3.10 (m, 1H), 3.71 (s, 3H), 4.95–5.15 (m,

2H), 5.91–6.12 (m, 1H); ^{13}C NMR δ 19.09, 19.28, 21.51, 21.71, 23.90, 26.17, 33.86, 34.76, 41.69, 52.01, 115.69, 137.65, 174.66, 180.50; FABMS *m/z* (relative intensity) 253 (MH^+, 6), 154 (100), 136 (79), 107 (27), 89 (28), 77 (25), 55 (15); HRMS calcd for $C_{14}H_{21}O_4$ *m/z* 253.1440. Found *m/z* 253.1447. Anal. calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.52; H, 7.89.

3.2.6. 2-(8-Carboxybicyclo[5.1.0]oct-8-yl)malonic acid monomethyl ester (6a). Electrochemical carboxylation of bicyclo[5.1.0]oct-8-ylideneacetic acid methyl ester (**4a**) (360 mg, 2 mmol) in MeCN gave 2-(8-carboxybicyclo-[5.1.0]oct-8-yl)malonic acid monomethyl ester (**6a**) (356 mg, 66%): mp 190–193 °C (ethyl acetate); IR ν 3600–2000 (broad), 1756, 1694 cm^{-1}; ^{1}H NMR δ 0.85–1.51 (m, 5H), 1.72–2.19 (m, 7H), 3.32 (s, 1H), 3.74 (s, 3H); ^{13}C NMR δ 25.33, 25.40, 27.85, 29.83, 29.95, 31.86, 33.68, 48.36, 51.71, 169.32, 169.64, 175.16; FABMS *m/z* (relative intensity) 271 (MH^+, 16), 253 (33), 154 (100), 136 (79), 107 (28), 89 (28), 77 (29), 55 (14); HRMS calcd for $C_{13}H_{19}O_6$ *m/z* 271.1182. Found *m/z* 271.1201. Anal. calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.85; H, 6.77.

3.2.7. 2-(8-Carboxybicyclo[5.1.0]oct-8-yl)malonic acid monoethyl ester (6b). Electrochemical carboxylation of bicyclo[5.1.0]oct-8-ylideneacetic acid ethyl ester (**4b**) (388 mg, 2 mmol) in MeCN gave 2-(8-carboxybicyclo-[5.1.0]oct-8-yl)malonic acid monoethyl ester (**6b**) (426 mg, 75%): mp 173–175 °C (ethyl acetate); IR ν 3600–2000 (broad), 1750, 1697 cm^{-1}; ^{1}H NMR δ 0.85–1.51 (m, 5H), 1.26 (t, J=6.93 Hz, 3H), 1.69–2.19 (m, 7H), 3.28 (s, 1H), 4.17 (q, J=6.93 Hz, 2H); ^{13}C NMR δ 12.99, 24.94, 27.44, 29.26, 29.29, 31.38, 33.16, 47.98, 59.84, 168.21, 169.11, 174.25; FABMS *m/z* (relative intensity) 285 (MH^+, 22), 267 (59), 154 (100), 136 (89), 107 (33), 89 (37), 77 (39), 55 (24); HRMS calcd for $C_{14}H_{21}O_6$ *m/z* 285.1338. Found *m/z* 285.1353. Anal. calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 59.06; H, 7.12.

3.2.8. 8-(1-Methoxycarbonylethyl)bicyclo[5.1.0]octane-8-carboxylic acid (5d). Electrochemical carboxylation of 2-bicyclo[5.1.0]oct-8-ylidenepropanoic acid methyl ester (**4d**) (388 mg, 2 mmol) in DMF gave 8-(1-methoxycarbonylethyl)bicyclo[5.1.0]octane-8-carboxylic acid (**5d**) (312 mg, 65%): mp 153–155 °C (ethyl acetate); IR ν 3600–2000 (broad), 1743, 1677 cm^{-1}; ^{1}H NMR δ 0.85–1.52 (m, 5H), 1.35 (d, J=6.93 Hz, 3H), 1.69–2.25 (m, 7H), 2.37 (q, J=6.93 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR δ 14.49, 25.90, 26.26, 28.36, 28.66, 30.50, 32.65, 33.62, 35.89, 36.79, 51.88, 175.02, 180.72; FABMS *m/z* (relative intensity) 241 (MH^+, 3), 154 (100), 136 (66), 107 (25), 89 (25), 77 (27), 69 (19), 55 (25), 41 (26); HRMS calcd for $C_{13}H_{21}O_4$ *m/z* 241.1440. Found *m/z* 241.1416. Anal. calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.95; H, 8.36.

3.2.9. 8-(1-Methoxycarbonylbut-3-enyl)bicyclo[5.1.0]-octane-8-carboxylic acid (5e). Electrochemical carboxylation of 2-bicyclo[5.1.0]oct-8-ylidenepent-4-enoic acid methyl ester (**4e**) (440 mg, 2 mmol) in DMF gave 8-(1-methoxycarbonylbut-3-enyl)bicyclo[5.1.0]octane-8-carboxylic acid (**5e**) (362 mg, 68%): mp 140–142 °C (pet. ether); IR ν 3600–2000 (broad), 1744, 1678 cm^{-1}; ^{1}H NMR δ 0.85–1.52 (m, 5H), 1.72–2.27 (m, 7H), 2.27–2.39 (m, 2H), 2.92–3.10 (m, 1H), 3.68 (s, 3H), 4.95–5.15 (m, 2H), 5.89–6.12 (m, 1H); ^{13}C NMR δ 26.29, 26.42, 28.36, 28.63, 30.84, 32.56, 33.75, 34.90, 36.91, 41.85, 51.92, 115.78, 137.59, 174.41, 180.47; FABMS *m/z* (relative intensity) 267 (MH^+, 69), 249 (100), 225 (54), 189 (26), 161 (25), 154 (27), 137 (35), 107 (27), 91 (40), 79 (35), 67 (27), 55 (25), 41 (37); HRMS calcd for $C_{15}H_{23}O_4$ *m/z* 267.1596. Found *m/z* 267.1601. Anal. calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33. Found: C, 67.47; H, 8.38.

3.3. Acid treatment of the carboxylated products

3.3.1. 2-(8-Methoxycarbonylbicyclo[5.1.0]oct-8-yl)-malonic acid dimethyl ester (7). 2-(8-Methoxycarbonyl-bicyclo[5.1.0]oct-8-yl)malonic acid dimethyl ester (**7**) was prepared in a 48% yield from 2-(8-carboxybicyclo-[5.1.0]oct-8-yl)malonic acid monomethyl ester (**6a**). To a solution of dicarboxylic acid **6a** (270 mg, 1 mmol) in methanol (5 mL) was added concentrated hydrochloric acid (3 mL). The mixture was heated under reflux for overnight, and then the solvent was evaporated and extracted with ethyl acetate (5 mL×3). The combined organic phases were washed successively with water, saturated brine and dried over $MgSO_4$. Filtration, concentration in vacuo and column chromatography on silica eluting with a mixture of ether/hexane (3:2) afforded 2-(8-methoxycarbonylbicyclo-[5.1.0]oct-8-yl)malonic acid dimethyl ester (**7**) (143 mg, 48%); IR (neat) ν 1751, 1741, 1727 cm^{-1}; ^{1}H NMR δ 0.85–1.52 (m, 5H), 1.79–2.18 (m, 7H), 3.38 (s, 1H), 3.65 (s, 3H), 3.77 (s, 6H); ^{13}C NMR δ 25.91, 28.41, 30.62, 32.54, 34.54, 48.84, 52.08, 52.58, 169.16, 173.55; EIMS *m/z* (relative intensity) 298 (M^+, 7), 266 (70), 239 (100), 234 (39), 207 (65), 202 (28), 179 (29), 175 (54), 147 (39), 119 (68), 91 (41), 79 (30), 59 (52); HRMS calcd for $C_{15}H_{22}O_6$ *m/z* 298.1416. Found *m/z* 298.1405.

3.3.2. 8-Carboxymethylbicyclo[5.1.0]octane-8-carboxylic acid (8). 8-Carboxymethylbicyclo[5.1.0]octane-8-carboxylic acid (**8**) was prepared in a 94% yield from 2-(8-carboxybicyclo[5.1.0]oct-8-yl)malonic acid monomethyl ester (**6a**). To a solution of dicarboxylic acid **6a** (270 mg, 1 mmol) in DMSO (5 ml) was added 6 M hydrochloric acid (3 mL). The mixture was heated under reflux for 30 h, and then the solvent was evaporated and extracted with ethyl acetate (5 mL×3). The combined organic phases were washed successively with water, saturated brine and dried over $MgSO_4$. Filtration and concentration in vacuo afforded 8-carboxymethylbicyclo[5.1.0]octane-8-carboxylic acid (**8**) (200 mg, 94%): mp 237–240 °C (ethyl acetate); IR ν 3600–2000 (broad), 1718, 1687 cm^{-1}; ^{1}H NMR δ 0.81–1.47 (m, 5H), 1.55–2.11 (m, 7H), 2.61 (s, 2H); ^{13}C NMR δ 24.21, 27.32, 28.36, 28.81, 29.22, 31.11, 172.43, 175.22; FABMS *m/z* (relative intensity) 213 (MH^+, 25), 195 (44), 154 (100), 136 (87), 107 (33), 89 (35), 77 (31); HRMS calcd for $C_{11}H_{17}O_4$ *m/z* 213.1127. Found *m/z* 213.1117. Anal. calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 61.98; H, 7.78.

3.3.3. 7-*endo*-Carboxymethylbicyclo[4.1.0]heptane-7-*exo*-carboxylic acid (9). To a solution of 2-(7-carboxy-bicyclo[4.1.0]hept-7-yl)malonic acid monoethyl ester (**3b**) (270 mg, 1 mmol) in DMSO (5 mL) was added 6 M hydrochloric acid (3 mL). The mixture was heated under reflux for 30 h, and then the solvent was evaporated and the

residue was extracted with ethyl acetate (5 mL×3). The combined organic phases were washed successively with water and saturated brine, and dried over $MgSO_4$. Evaporation of the solvent in vacuo afforded 164 mg (83%) of 7-*endo*-carboxymethylbicyclo[4.1.0]heptane-7-*exo*-carboxylic acid (**9**) whose spectral data are identical with reported values.[24] Mp 191–194 °C (lit.[24] 193 °C); IR ν 3600–2000 (broad), 1717, 1686 cm^{-1}; ^1H NMR (DMSO) δ 1.10–1.50 (m, 6H), 1.60–1.75 (m, 2H), 1.85–2.05 (m, 2H), 2.60 (s, 2H); ^{13}C NMR δ 18.02, 20.84, 21.49, 26.46, 30.02, 173.37, 176.80; FABMS *m/z* (relative intensity) 199 (MH^+, 17), 181 (17), 154 (100), 136 (60), 107 (19), 89 (19), 77 (23). Anal. calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.36; H, 7.16.

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