

Fluorination of Secondary and Primary Alcohols by Thermal Decomposition of Electrochemically Generated Alkoxy Triphenylphosphonium Tetrafluoroborates

Hatsuo MAEDA, Takashi KOIDE, Sayaka MATSUMOTO, and Hidenobu OHMORI*

Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565, Japan.

Received March 13, 1996; accepted April 12, 1996

Replacement of hydroxyl groups in secondary and primary alcohols (1) with a fluorine atom arising from tetrafluoroborate anion has been performed by the electrochemical formation of alkoxy triphenylphosphonium tetrafluoroborates (2) from 1, followed by their thermal decomposition. The procedure is quite simple, involving: (1) constant-current electrolysis of a mixture of 1, Ph_3P , and $\text{Ph}_3\text{PH}\cdot\text{BF}_4$ in CH_2Cl_2 in an undivided cell; (2) refluxing a tetrahydrofuran or dioxane solution of the residue afforded by evaporation of the solvent *in vacuo* after the electrolysis. Cyclic secondary alcohols such as 3β -hydroxy steroids and 2-adamantanol are transformed into the corresponding fluorides in satisfactory yields when the geometry of the leaving group in 2 is suitable for the substitution or an elimination process for 2 to give an alkene is stereochemically forbidden. The fluorination of steroidal alcohols and 4-phenyl-1-cyclohexanol proceeded with complete inversion, demonstrating that a fluorine atom from the tetrafluoroborate anion attacks from the side opposite to the phosphonium moiety in 2 *via* an $\text{S}_{\text{N}}2$ mechanism rather than an $\text{S}_{\text{N}}1$ mechanism. The fluorination of acyclic secondary and primary alcohols was performed by the present method in reasonable yields, although the reaction for the latter required more forcing conditions, such as refluxing in dioxane.

Key words alcohol fluorination; alkoxy triphenylphosphonium tetrafluoroborate; pyrolysis; triphenylphosphine; constant-current electrolysis

During our study on the nucleophilic substitution reactions of alkoxy triphenylphosphonium ions prepared electrochemically from an alcohol and Ph_3P ,¹⁾ the thermal decomposition of aryl diazonium tetrafluoroborates into the corresponding aryl fluorides (so-called Schiemann reaction)²⁾ attracted our attention, since the phosphonium tetrafluoroborates are expected to undergo similar reactions, in which $\text{Ph}_3\text{P}=\text{O}$ functions as an excellent leaving group, as N_2 does in the Schiemann reaction. Fluorination with tetrafluoroborate anion as a fluoride source seems of interest from the standpoint of synthetic organic chemistry, since such reactions will not involve the generation of rather intractable HF, and various tetrafluoroborate salts are commercially available and inexpensive. Only a limited number of examples of the introduction of a fluorine atom with tetrafluoroborate anions, in addition to the Schiemann reaction, have appeared in the literature.³⁻⁷⁾ Among them, the transformation of 2,3:5,6-di-*O*-isopropylidene- α -D-mannofuranose into the corresponding glycosyl fluoride by a modified Mitsunobu reaction with Ph_3P , diethyl azodicarboxylate, and triethyloxonium tetrafluoroborate,⁷⁾ in which the corresponding alkoxy triphenylphosphonium tetrafluoroborate was claimed to be an intermediate, strongly encouraged us to examine the possibility of the thermal decomposition of an electrochemically generated alkoxy triphenylphosphonium tetrafluoroborate as a novel tool to replace a hydroxyl group with a fluorine atom arising from the borate anion. Here we wish to report that the constant-current electrolysis of Ph_3P in the presence of a secondary or a primary alcohol in CH_2Cl_2 containing $\text{Ph}_3\text{PH}\cdot\text{BF}_4$ as a supporting electrolyte, followed by pyrolysis of the crude product in tetrahydrofuran (THF) or dioxane, is available for the transformation of the alcohol into the corresponding fluoride.

Results and Discussion

In order to examine whether an alkoxy triphenylphosphonium tetrafluoroborate will undergo thermal decomposition into the corresponding alkyl fluoride or not, the phosphonium ion **2a**, prepared electrochemically from β -cholestanol (**1a**) and isolated as previously reported,¹⁾ was chosen as a model compound and heated in CHCl_3 , THF, benzene, CH_3CN , 1,2-dimethoxyethane (DME), or dioxane (Chart 1). The results are summarized in Table 1.

When a solution of **2a** in CHCl_3 was refluxed, TLC analysis demonstrated that **2a** was smoothly decomposed even under mild conditions, namely, at 61°C (run 1). Although an olefinic product **4** was predominantly formed in 81% yield by the pyrolysis, a trace amount of the fluorinated product **3a** was also obtained, indicating that the pyrolysis of alkoxy triphenylphosphonium tetrafluoroborates could be useful as a tool to prepare alkyl fluorides, as we had expected. Utilizing THF as a solvent facilitated the formation of **3a**, which was obtained in a satisfactory yield of 54% along with 35% of **4** (run 2). The reactions in benzene, DME, and dioxane were also found to give **3a**, although the yields were not as good as in THF and the main product was **4** (runs 3, 5, and 6).

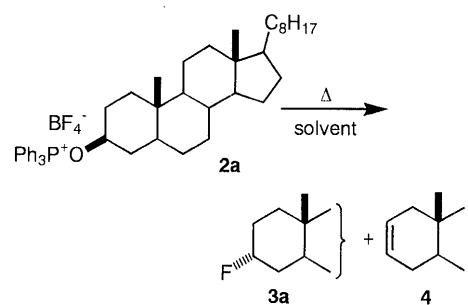


Chart 1

* To whom correspondence should be addressed.

Table 1. Results of Thermal Decomposition of the Alkoxy Triphenylphosphonium Tetrafluoroborate (**2a**) Derived from β -Cholesterol (**1a**)^{a)}

| Run | Solvent | Condition | Reaction time | Yield ^{b)} (%) of | |
|------------------|--------------------|-----------|---------------|----------------------------|------------------|
| | | | | 3a | 4 |
| 1 | CHCl ₃ | Reflux | 2 h | Trace | 81 |
| 2 | THF | Reflux | 2.5 h | 54 | 35 |
| 3 | Benzene | Reflux | 1 h | 26 | 68 |
| 4 | CH ₃ CN | Reflux | 80 min | — | 75 |
| 5 | DME | Reflux | 30 min | 33 | 51 |
| 6 | Dioxane | Reflux | 15 min | 6 | 89 |
| 7 | THF | At 40 °C | 24 h | 52 | 27 |
| 8 | Benzene | At 40 °C | 24 h | 46 | 35 |
| 9 | Dioxane | At 40 °C | 20 h | 45 | 45 |
| 10 | Dioxane | At 65 °C | 45 min | 47 | 49 |
| 11 ^{c)} | THF | Reflux | 1 h | 54 ^{e)} | 32 ^{e)} |
| 12 ^{d)} | THF | Reflux | 50 min | 52 ^{e)} | 32 ^{e)} |

a) The reaction was carried out on the isolated **2a**. b) Isolated yield based on **2a**. c, d) The reaction was carried out with unpurified **2a** obtained by the electrolysis for **1a** with and without aqueous work-up, respectively. For details, see the text. e) Isolated yield based on **1a** subjected to the electrolysis.

The reaction in CH₃CN gave **4** as a sole product (run 4). The decomposition of **2a** was sluggish at 40 °C in THF, benzene, or dioxane, requiring a much longer time to complete (runs 7–9). However, the formation of **3a** from **2a** in benzene or dioxane was much improved as compared with that under reflux, with yields comparable to that obtained by the reaction under reflux in THF (runs 8 and 9). In the case of THF, no difference in the yield of **3a** was observed between the reactions at 40 °C and under reflux (run 7). In dioxane at 65 °C, **2a** entered the reaction course more effectively, giving **3a** in 47% yield after only 45 min (run 10). From these results, refluxing in THF seems to be the condition of choice for the preparation of **3a** from **2a**.

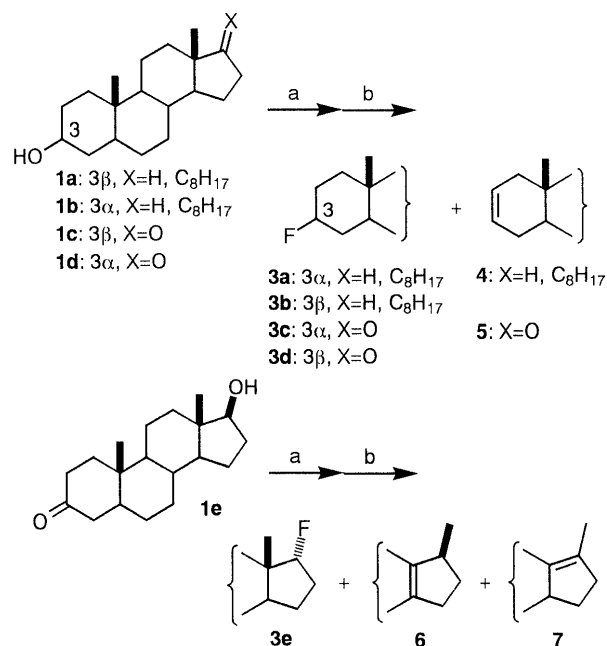
Runs 11 and 12 show the results for the reaction of unpurified **2a** obtained without any isolation procedure after the electrolysis of a mixture of **1a**, Ph₃P, and Ph₃PH·BF₄ in CH₂Cl₂. When purified **2a**, obtained through aqueous work-up of the electrolyte, drying the organic layer, and removal of the solvent *in vacuo*, was heated under reflux in THF, **3a** was obtained in 54% yield based on **1a** used for the electrolysis, accompanied with **4** in 32% yield (run 11). A similar result was noted in the pyrolysis of another kind of unpurified **2a** obtained just by evaporating the solvent *in vacuo* after the electrolysis (run 12). Since **2a** was isolated in 76% yield after the electrolysis,¹⁾ these results are better than that obtained with isolated **2a**, with respect to overall yield of **3a** from **1a**: the yield is calculated to be 41% in the stepwise process, that is, the electrolysis, the isolation, and the pyrolysis. From the synthetic point of view, the simplicity of the procedure in run 12 seems to be useful and implies that the present reaction would be applicable to the preparation of alkyl fluorides from alcohols, even when the corresponding phosphonium ions are unstable or difficult to isolate in pure forms. Thus, the transformation of various alcohols into the corresponding alkyl fluorides was conducted by using the procedure of run 12. The results are summarized in Table 2.

The success in the present fluorination of 3-hydroxy steroids, including **1a** (Chart 2), probably depended on

Table 2. Results of Transformation of Alcohols into Alkyl Fluorides by the Sequence of Constant-Current Electrolysis and Pyrolysis^{a)}

| Run | Alcohol | Reaction time ^{b)} | Product (%) ^{c)} | |
|------------------|--------------------------|-----------------------------|-----------------------------|----------------------------|
| 1 | 1a | 50 min | 3a (52) | 4 (32) |
| 2 | 1b | 15 min | 3b (2) | 4 (79) |
| 3 | 1c | 45 min | 3c (55) | 5 (31) |
| 4 | 1d | 40 min | 3d (9) | 5 (73) |
| 5 | 1e | 36 h | 3e (5) | 6 + 7 (75) |
| 6 | <i>trans</i> - 1f | 6 h | <i>cis</i> - 3f (29) | 8 (57) |
| 7 | <i>cis</i> - 1f | 3 h | | 8 (68) |
| 8 | 1g | 40 min | 3g (5) | 9 (61) |
| 9 | 1h | 45 min | 3h (73) | |
| 10 | 1i | 1 h | 3i (46) | 10 (24) |
| 11 | 1j | 75 min | 3j (38) | 11 + 12 (27) |
| 12 ^{d)} | 1k | 1 h | 3k (37) | 13 (14) |
| 13 ^{d)} | 1l | 4 h | 3l (30) | 14 (18) |

a) A mixture of **1**, Ph₃P, and Ph₃P·BF₄ (3 mmol each) was subjected to the electrolysis (30 mA, 3 F/mol against **1**). b) Required to complete the decomposition of the unpurified alkoxy phosphonium ions formed in the electrolysis. c) Isolated yields based on the amount of **1** subjected to the electrolysis. d) A mixture of **1** (3 mmol), Ph₃P (4 mmol), and Ph₃P·BF₄ (4 mmol) was subjected to the electrolysis (30 mA, 3.5 F/mol against **1**).



the stereochemistry at the C3 position. Although **1a** was transformed into **3a** in 52% yield by the sequence of electrolysis and pyrolysis as mentioned above (run 1 in Table 2), the reaction sequence for **1b**, an epimer of **1a**, was not successful in generating the corresponding fluorosteroid **3b**, which was obtained in only 2% yield together with 79% of the eliminated product **4** (run 2). In the case of epiandrosterone (**1c**), the transformation into **3c** was achieved in 55% yield, while the reaction sequence for androsterone (**1d**) gave **3d** and **5** in 9 and 73% yields, respectively (runs 3 and 4). These results demonstrate that the present fluorination will be useful for steroidal alcohols with the functional groups occupying equatorial positions, but axial hydroxyl groups in the steroids will result in

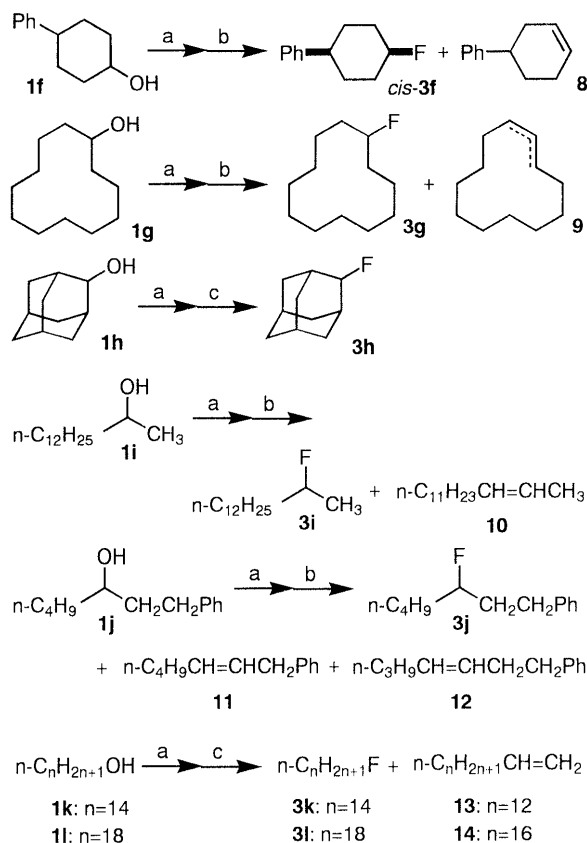


Chart 3

preferential formation of olefinic by-products over fluorinated products. The observed trend is not inherent in the present method, since difficulty has been well recognized in fluorinating steroidal secondary alcohols when the geometry of the leaving groups is suitable for elimination rather than fluorination. In fact, fluorination of these 3-hydroxy steroids with diethylaminosulfur trifluoride (DAST)⁸⁾ showed a similar tendency: **3a** (43%) and **4** (32%) from **1a**⁹⁾; **3c** (47%) and **5** (44%) from **1c**¹⁰⁾; **3d** (14%) and **5** (83%) from **1d**.¹⁰⁾ Thus, the present fluorination has turned out to give results better than or comparable to those obtained with a widely used fluorinating reagent for alcohols. When the present fluorination was conducted on stanolone (**1e**), the thermal decomposition of the corresponding alkoxy phosphonium ion was remarkably sluggish. The pyrolysis was completed after 36 h, giving **3e** in only 5% yield due to extensive formation of olefinic by-products **6** and **7** in 75% yield (run 5), although it was reported that the hydroxyl group in **1e** was replaced with fluorine in 39% yield through the reaction with DAST.⁹⁾ It should be mentioned here that the present fluorination proceeded with complete inversion of configuration at the carbon bearing a hydroxyl group. The results suggest that in the process of the pyrolysis of an alkoxy triphenylphosphonium salt, a fluorine atom from the tetrafluoroborate anion will attack from the side opposite to the phosphonium moiety *via* an *S_N2* mechanism rather than an *S_N1* mechanism.

The present fluorination with electrolysis followed by

the pyrolysis was also performed on simple secondary and primary alcohols (Chart 3). When *trans*-**1f** was subjected to the reaction, *cis*-**3f** was obtained in 29% yield as a sole fluorinated product, along with 57% of **8**, while *cis*-**1f** was transformed only into **8** in 68% yield under the same conditions (runs 6 and 7). In the case of **1g**, a pronounced preference for elimination rather than fluorination was noted (run 8). These results demonstrate that the present fluorination of a monocyclic alcohol, even with a conformational locking group, is unsatisfactory, probably due to a lower population of the preferred conformation in such a system at the temperature required for the decomposition of the alkoxy triphenylphosphonium ion. The thermal decomposition of the phosphonium ion generated electrochemically from **1h** required more forcing conditions. Thus, refluxing in dioxane instead of THF prompted the decomposition, giving a fluorinated product (**3h**) in a good yield (73%, run 9). This result is reasonable since the formation of the eliminated product in the system is forbidden.

The electrolysis of **1i** or **1j** followed by pyrolysis under reflux in THF gave **3i** or **3j**, respectively, as the fluorinated product in a reasonable yield, although the eliminated product was also obtained in each case (runs 10 and 11).¹¹⁾ When the crude product obtained by electrolysis of **1k** or **1l** was refluxed in THF, TLC analysis showed that the corresponding phosphonium ion remained intact even after prolonged heating. However, the formation of a fluorinated product was observed on refluxing a dioxane solution of the electrolysis product, and **1k** and **1l** were converted into **3k** and **3l** in 37 and 30% yields, respectively (runs 12 and 13). Thus, the present method has turned out to be more effective for replacing hydroxyl groups in acyclic alcohols with a fluorine atom than it was for monocyclic alcohols such as **1f** and **1g**.

The fluorination of tertiary, benzylic, or allylic alcohols was not attempted in the present study, since the formation of the corresponding alkoxy triphenylphosphonium ions was not recognized on electrolysis under essentially the same conditions, probably due to instability. But it can be expected that electrolysis of such an alcohol, Ph_3P , and a tetrafluoroborate salt as a supporting electrolyte under proper conditions will give a fluorinated compound without pyrolysis, providing direct access for the preparation of the corresponding alkyl fluoride. Further studies are under way.

Experimental

Infrared (IR) spectra were taken on a JASCO VALOR-III spectrometer. ¹H- and ¹³C-NMR spectra were obtained at 200 and 67.8 MHz on Varian VXR-200 and JEOL EX-270 spectrometers, respectively, in CDCl_3 with tetramethylsilane (TMS) as an internal standard. For column chromatography, SiO_2 (Wakogel C-200) was used. Constant-current electrolysis (CCE) was carried out with a Hokuto Denko HA301, HA104, or HA105 potentiostat/galvanostat connected with a Hokuto Denko HF 201 coulomb/amperehour meter.

Materials $\text{Ph}_3\text{PH}\cdot\text{BF}_4$ was obtained by the addition of 42% HBF_4 to a solution of Ph_3P in CH_3CN ; the resulting precipitate was filtered off, recrystallized from CH_3CN , and dried *in vacuo*. Each isomer of 4-phenyl-1-cyclohexanol (**1f**) was obtained by reduction of 4-phenyl-1-cyclohexanone with LiAlH_4 in THF, followed by chromatographic separation. Compound **1j** was prepared by the reaction of 3-phenylpropionaldehyde and *n*-BuLi. All other chemicals were of reagent

grade, and were used without further purification. CH_2Cl_2 was distilled from P_2O_5 and stored over molecular sieves 4A. Dried THF and dioxane were purchased from Kanto Chemical Co., Inc., stored over molecular sieves 4A, and used without further purification. All other solvents were dried by distillation in the usual manner prior to use.

General Procedure for the Fluorination of Alcohols by Electrolysis Followed by Pyrolysis A CH_2Cl_2 solution (30 ml) of Ph_3P (3 or 4 mmol), $\text{Ph}_3\text{PH} \cdot \text{BF}_4$ (3 or 4 mmol), and **1** (3 mmol) in an undivided cell equipped with a graphite plate anode (12.5 cm^2) and a Pt foil cathode (4.0 cm^2) was deoxygenated by bubbling N_2 for 20 min, and then subjected to CCE (30 mA) at room temperature under an N_2 atmosphere. After 3 or 3.5 F/mol (vs. **1**) had been passed, the solvent was removed under reduced pressure. The residue was taken up in THF or dioxane (50 ml) and the resulting mixture was heated under reflux. When TLC analysis indicated that alkoxy triphenylphosphonium tetrafluoroborate was totally consumed, the mixture was cooled to room temperature. In the case of the pyrolysis in THF, after the removal of the solvent under reduced pressure, the residue was poured into brine (50 ml) and extracted with ether (50 ml \times 3); the combined organic layer was dried over MgSO_4 , then concentrated under reduced pressure, and the residue was subjected to silica gel column chromatography (*n*-hexane or *n*-hexane-ethyl acetate) to give the products. In the case of the pyrolysis in dioxane, the reaction mixture was poured into brine and extracted with ethyl acetate (50 ml) and ether (50 ml \times 2); the combined organic layer was washed with brine (200 ml) and treated in a similar manner to the above to afford the products. The products **3a**,¹² **3b**,¹² **3c**,¹⁰ **3d**,¹⁰ **3e**,¹⁰ **4**,¹ **5**,¹ **6**,¹⁰ **7**,¹⁰ **9**, **13**, and **14** were identified by comparison of their spectroscopic data with those described in the cited references or with those of commercial authentic samples. Other products including the known compounds **3g**¹³ and **3h**^{14,15} gave satisfactory physical data as shown below.

cis-1-Fluoro-4-phenylcyclohexane (3f) $^1\text{H-NMR}$ δ : 7.35–7.14 (5H, m), 4.91 (1H, d of brs, $J_{\text{HF}} = 49.2\text{ Hz}$), 2.61–2.49 (1H, m), 2.27–1.43 (8H, m). $^{13}\text{C-NMR}$ δ : 147.00 (s), 128.39 (2C, d), 126.79 (2C, d), 126.07 (d), 88.20 (dd, $J_{\text{CF}} = 167.2\text{ Hz}$), 43.43 (d), 31.27 (t), 30.96 (t), 27.94 (2C, t). HR-MS m/z : Calcd for $\text{C}_{12}\text{H}_{15}\text{F}$: 178.1159. Found: 178.1156.

4-Phenyl-1-cyclohexene (8) $^1\text{H-NMR}$ δ : 7.37–7.14 (5H, m), 5.76 (2H, brs), 2.84–2.75 (1H, m), 2.29–2.13 (4H, m), 2.00–1.60 (2H, m). $^{13}\text{C-NMR}$ δ : 147.35 (s), 128.35 (2C, d), 126.99 (d), 126.90 (2C, d), 126.79 (d), 125.96 (d), 40.16 (d), 33.42 (t), 29.72 (t), 25.91 (t). HR-MS m/z : Calcd for $\text{C}_{12}\text{H}_{14}$: 158.1096. Found: 158.1103.

Fluorocyclododecane (3g) $^1\text{H-NMR}$ δ : 4.72 (1H, d of m, $J_{\text{HF}} = 54.4\text{ Hz}$), 1.90–1.20 (22H, m). $^{13}\text{C-NMR}$ δ : 92.50 (dd, $J_{\text{CF}} = 164.8\text{ Hz}$), 30.06 (t), 29.76 (t), 24.12 (2C, t), 23.81 (t), 23.27 (2C, t), 23.14 (2C, t), 20.59 (t), 20.49 (t). Anal. Calcd for $\text{C}_{12}\text{H}_{23}\text{F}$: C, 77.36; H, 12.44. Found: C, 77.48; H, 12.37.

2-Fluoroadamantane (3h) $^1\text{H-NMR}$ δ : 4.69 (1H, d of brs, $J_{\text{HF}} = 50.4\text{ Hz}$), 2.25–1.50 (14H, m). $^{13}\text{C-NMR}$ δ : 95.61 (dd, $J_{\text{CF}} = 178.2\text{ Hz}$), 37.23 (t), 35.81 (t), 35.67 (t), 32.97 (d), 32.70 (d), 31.48 (2C, t), 27.24 (d), 26.92 (d). HR-MS m/z : Calcd for $\text{C}_{10}\text{H}_{15}\text{F}$: 154.1159. Found: 154.1154.

2-Fluorotetradecane (3i) $^1\text{H-NMR}$ δ : 4.64 (1H, d of m, $J_{\text{HF}} = 50.4\text{ Hz}$), 1.74–1.38 (3H, m), 1.31 (3H, dd, $J = 23.9, 6.8\text{ Hz}$), 1.26 (19H, s), 0.88 (3H, t, $J = 6.8\text{ Hz}$). $^{13}\text{C-NMR}$ δ : 91.09 (dd, $J_{\text{CF}} = 163.5\text{ Hz}$), 36.99 (dt, $J_{\text{CF}} = 20.8\text{ Hz}$), 31.97 (t), 29.70 (3C, t), 29.59 (t), 29.52 (t), 29.42 (t), 25.18 (t), 25.10 (t), 22.73 (t), 21.03 (dq, $J_{\text{CF}} = 23.2\text{ Hz}$), 14.14 (q). Anal. Calcd for $\text{C}_{14}\text{H}_{29}\text{F}$: C, 77.71; H, 13.51. Found: C, 77.79; H, 13.35.

2-Tetradecene (10) obtained as a mixture of *E*- and *Z*-isomers. IR (KBr): 1656 and 1642 cm^{-1} . $^1\text{H-NMR}$ δ : 5.44–5.40 (2H, m), 2.10–1.90 (2H, m), 1.66–1.55 (3H, m), 1.26 (18H, brs), 0.88 (3H, t, $J = 6.3\text{ Hz}$). $^{13}\text{C-NMR}$ δ : 131.70 (0.67C, d), 130.91 (0.33C, d), 124.49 (0.67C, d),

123.54 (0.33C, d). HR-MS m/z : Calcd for $\text{C}_{14}\text{H}_{28}$: 196.2192. Found: 196.2189.

3-Fluoro-1-phenylheptane (3j) $^1\text{H-NMR}$ δ : 7.34–7.14 (5H, m), 4.48 (1H, d of m, $J_{\text{HF}} = 48.9\text{ Hz}$), 2.90–2.60 (2H, m), 2.02–1.25 (6H, m), 0.90 (3H, t, $J = 6.8\text{ Hz}$). $^{13}\text{C-NMR}$ δ : 141.65 (s), 128.44 (3C, d), 125.92 (2C, d), 93.48 (dd, $J_{\text{CF}} = 167.0\text{ Hz}$), 37.03 (dt, $J_{\text{CF}} = 22.0\text{ Hz}$), 34.91 (dt, $J_{\text{CF}} = 20.8\text{ Hz}$), 31.46 (dt, $J_{\text{CF}} = 4.9\text{ Hz}$), 27.29 (dt, $J_{\text{CF}} = 3.7\text{ Hz}$), 22.61 (t), 13.98 (q). HR-MS m/z : Calcd for $\text{C}_{13}\text{H}_{19}\text{F}$: 194.1472. Found: 194.1465.

1-Phenyl-2-heptene (11) and 1-Phenyl-3-heptene (12) Inseparable mixture¹¹: IR (KBr): 1604 cm^{-1} . $^1\text{H-NMR}$ δ : 7.33–7.13 (5H, m), 5.57–5.50 (0.83H, m), 5.45–5.37 (1.17H, m), 3.38 (0.21H, d, $J = 5.6\text{ Hz}$), 3.35 (0.62H, d, $J = 5.6\text{ Hz}$), 2.67 (1.17H, t, $J = 7.8\text{ Hz}$), 2.41–1.90 (3H, m), 1.44–1.24 (3H, m), 0.95–0.83 (3H, m). HR-MS m/z : Calcd for $\text{C}_{13}\text{H}_{18}$: 174.1409. Found: 174.1408.

1-Fluorotetradecane (3k) $^1\text{H-NMR}$ δ : 4.43 (2H, dt, $J_{\text{HF}} = 47.4\text{ Hz}$ and $J = 6.1\text{ Hz}$), 1.88–1.55 (2H, m), 1.26 (22H, s), 0.88 (3H, t, $J = 6.2\text{ Hz}$). $^{13}\text{C-NMR}$ δ : 84.10 (dd, $J_{\text{CF}} = 163.5\text{ Hz}$), 31.97 (t), 30.48 (dt, $J_{\text{CF}} = 19.5\text{ Hz}$), 29.71 (3C, t), 29.62 (t), 29.58 (t), 29.42 (t), 29.31 (t), 25.23 (t), 25.16 (t), 22.72 (t), 14.07 (q). HR-MS m/z : Calcd for $\text{C}_{14}\text{H}_{29}\text{F}$: 216.2255. Found: 216.2256.

1-Fluorooctadecane (3l) $^1\text{H-NMR}$ δ : 4.44 (2H, dt, $J_{\text{HF}} = 49.2\text{ Hz}$ and $J = 6.3\text{ Hz}$), 1.78–1.58 (2H, m), 1.27 (30H, s), 0.88 (3H, t, $J = 6.6\text{ Hz}$). $^{13}\text{C-NMR}$ δ : 84.22 (dd, $J_{\text{CF}} = 163.6\text{ Hz}$), 31.99 (t), 30.48 (dt, $J_{\text{CF}} = 19.6\text{ Hz}$), 29.75 (8C, t), 29.61 (t), 29.58 (t), 29.42 (t), 29.31 (t), 25.20 (dt, $J_{\text{CF}} = 6.1\text{ Hz}$), 22.73 (t), 14.12 (q). HR-MS m/z : Calcd for $\text{C}_{18}\text{H}_{37}\text{F}$:

Acknowledgment This work was supported in part by Grants-in-Aid for Scientific Research (06772070 and 07772099) from the Ministry of Education, Science, Sports, and Culture, Japan.

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