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Phosphorofluoridic Acid Ammonium Salts and Acids: Synthesis, NMR Properties, and Application as Acid Catalysts

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ABSTRACT: *Phosphoric acid alkyl diphenyl esters were prepared by reacting diphenyl phosphoryl chloride with alcohols in the presence of amines, and then subjected to fluorinative hydrolysis with Bu_4NF to give phosphorofluoridic acid ammonium salt monoesters in moderate to high yields. The salts were converted to the corresponding acids by treatment with Amberlyst 15. The NMR properties of a series of organophosphorus compounds are presented. The catalytic activities of the acids for the condensation reaction of α-bromobutanoic acid and 3-hexyne-2-ol were tested.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:417–425, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20700

INTRODUCTION

Introduction of a fluorine atom to organophosphorus compounds adds unique properties to the resulting compounds [1–3]. For example, fluorinated phosphoric acids are expected to be more acidic than the nonfluorinated corresponding acids, whereas fluorinated phosphorates are less basic and less nucleophilic than the corresponding phosphorates. The stability of fluorinated phosphorates is higher than that of other halogen-substituted phosphorates. Therefore, phosphoric acid derivatives bearing a P—F bond have been used as key intermediates to lead to biologically interesting molecules. Additionally, a ^{19}F nucleus can be a probe for disclosing some interaction between phosphoric acid derivatives and biologically relevant molecules. Metal fluorides such as KF [4,5] and AgF [6,7], hydrogen fluoride/amine complexes [8,9], and diethylaminosulfur trifluoride (DAST) [10] are used as fluorinating agents for phosphorus chlorides and esters. Tetrabutylammonium fluoride (TBAF) has also been used to introduce fluorine atom to the phosphorus atom [5]. TBAF-*t*-BuOH adduct has recently been applied to the fluorination of phosphoryl chlorides [11]. Despite recent progress on the introduction of fluorination, the applicability of these methods is still limited, and new types of fluorinated organophosphorus compounds are demanded. In this regard, in our studies on compounds with P=Se bonds [12–22], we also found that phosphoric acid phenyl esters undergo fluorinative hydrolysis with a THF solution of TBAF [23]. We report herein the details of this reaction leading to phosphorofluoridic acid ammonium salt monoesters and their conversion to the corresponding acids. The application of these acids to the condensation reaction of carboxylic acids and alcohols is described.

RESULTS AND DISCUSSION

Initially, phosphoric acid alkyl diphenyl esters **3** were synthesized by reacting diphenyl phosphoryl chloride (**1**) with alcohols **2** (Table 1). As a combination of a solvent and base, THF/Et_3N or

Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

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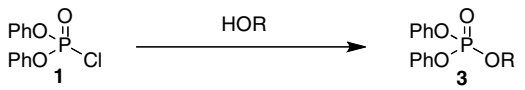
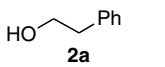
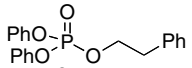
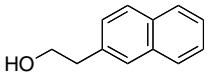
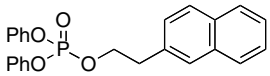
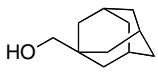
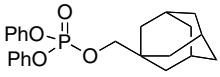
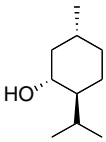
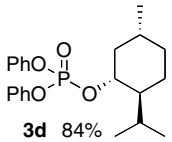
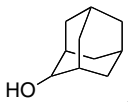
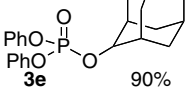
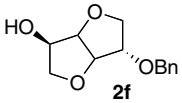
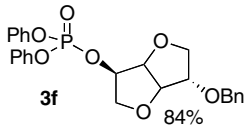
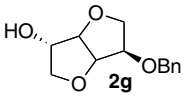
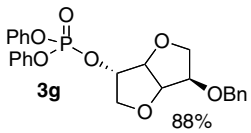
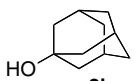
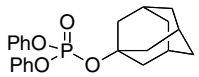
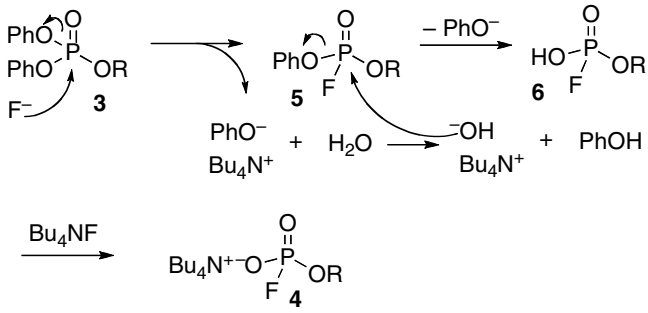
TABLE 1 Phosphorylation of Alcohols



Entry	Alcohol 2	Conditions	Yield
1	 **2a**	DMAP CH_2Cl_2 rt, 6 h	 **3a** 87%
2	 **2b**	Et_3N THF reflux 8 h	 **3b** 95%
3	 **2c**	DMAP CH_2Cl_2 rt 5 h	 **3c** 86%
4	 **2d**	DMAP CH_2Cl_2 $Ti(OiPr)_4$ (10 mol%) rt 2 h	 **3d** 84%
5	 **2e**	DMAP CH_2Cl_2 rt 6 h	 **3e** 90%
6	 **2f**	DMAP CH_2Cl_2 rt 5 h	 **3f** 84%
7	 **2g**	DMAP CH_2Cl_2 rt 6 h	 **3g** 88%
8	 **2h**	DMAP CH_2Cl_2 rt 5 h	 **3h** 86%

CH_2Cl_2/DMAP was used [24]. The reaction in the presence of Et_3N in THF required reflux temperature (entry 2), whereas the reaction with DMAP as a base in CH_2Cl_2 was complete at room temperature (entries 1, 3–8). As primary alcohols, 2-phenylethyl (**2a**) [25], 2-naphthylethyl (**2b**), and adamantylmethyl (**2c**) alcohols, as secondary alcohols, (l)-menthol (**2d**), 2-adamantanol (**2e**), and *O*-benzyl dianhydro-D-glucitols (**2f**) and (**2g**), and as a tertiary alcohol, 1-adamantanol, were used. No difference was observed in the efficiency of the condensation reactions between these alcohols **2** and phosphoryl chloride **1**.

Next, phosphoric esters **3** were stirred with TBAF in THF at room temperature. The signals due to the starting esters **3** gradually disappeared

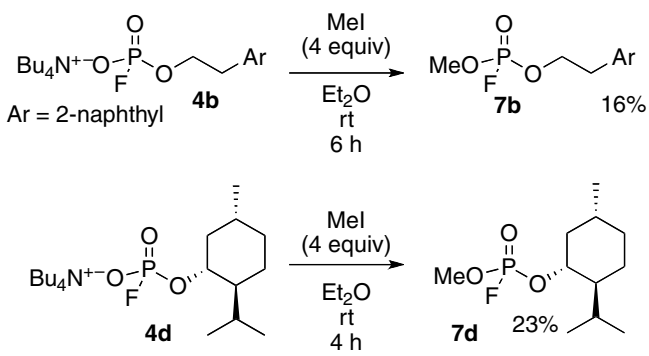


SCHEME 1

and new doublet signals corresponding to phosphorus atoms bearing a fluorine atom became larger in ^{31}P NMR spectra of the reaction mixture. When the signals due to **3** had completely disappeared, which required 5–20 h, the reaction mixture was poured onto H_2O and initially extracted with Et_2O. The aqueous layer was then extracted with CH_2Cl_2 and the organic layers were dried over $MgSO_4$, filtered, and concentrated to give phosphorofluoridic acid salt monoesters **4**. Generally, with this workup, the salts were efficiently isolated with a purity of greater than 90%. Excess TBAF was removed by extracting a CH_2Cl_2 solution of **4** with aqueous solution of NaOH several times.

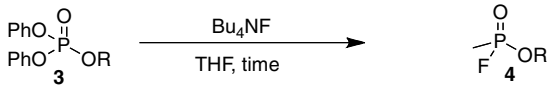
A plausible reaction pathway for the reaction in Table 2 is proposed in Scheme 1. Fluoride ion may initially attack the phosphorus atom in **3**, followed by the elimination of phenolate ion to generate phosphoryl fluorides **5**. The fluorides **5** were then subjected to the substitution reaction with hydroxyl ion generated from the phenolate ion and H_2O to form acids **6**, which are further deprotonated to lead to ammonium salts **4**.

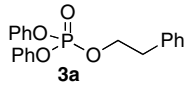
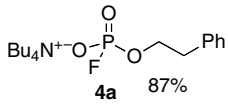
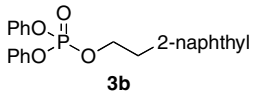
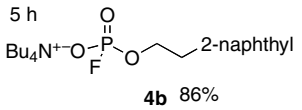
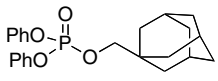
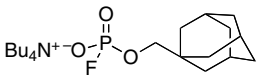
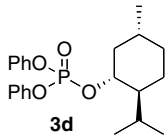
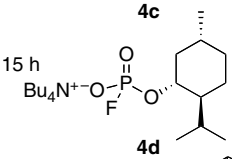
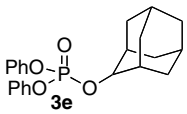
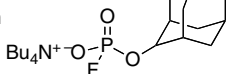
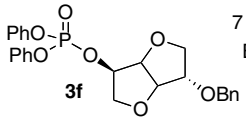
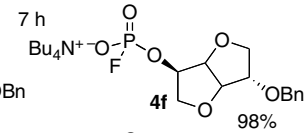
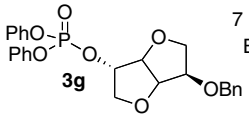
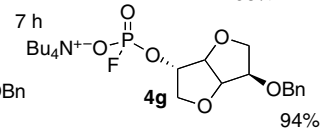
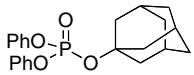
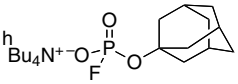
Some of the salts were reacted with methyl iodide and proton sources. Salts **4b** and **4d** were reacted with methyl iodide, with Et_2O as a solvent (Scheme 2). Even in the reaction with excess methyl



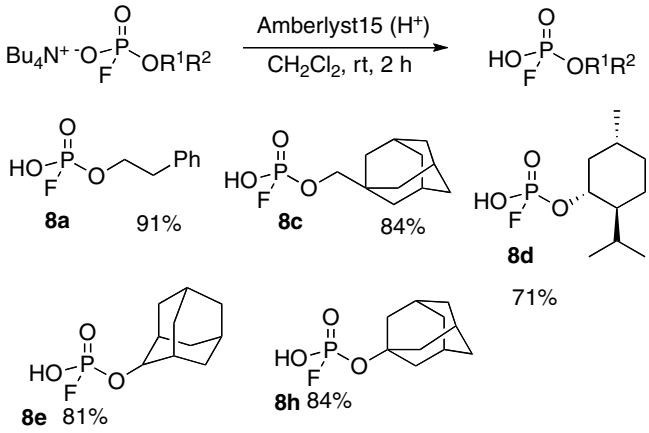
SCHEME 2

TABLE 2 Fluorinative Hydrolysis of Phosphoric Acid Diphenyl Esters



Entry	Alcohol 2	Time	Yield
1	 **3a**	16 h	 **4a** 87%
2	 **3b**	5 h	 **4b** 86%
3	 **3c**	8 h	 **4c** 63%
4	 **3d**	15 h	 **4d** 70%
5	 **3e**	8 h	 **4e** 98%
6	 **3f**	7 h	 **4f** 98%
7	 **3g**	7 h	 **4g** 94%
8	 **3h**	20 h	 **4h** 100%

iodide, methylation was not efficient and the methylated products **7** were obtained in only low yields, although the salts were completely dissolved in Et_2O and the reaction mixture was homogeneous. Acid hydrolysis of the salts **4** with an Et_2O solution of HCl also proceeded sluggishly and gave the desired acids in moderate yields. Instead, the salts **4** were stirred with Amberlyst 15 in CH_2Cl_2 for 2 h (Scheme 3). Filtration and concentration of the reaction mixture gave the desired acids **8** in good to excellent yields. Much less attention has recently been paid to phosphorofluoridic acids with simple carbon skeletons [2,26], but phosphorofluoridic acid moieties are



SCHEME 3

found in biologically important molecules [3,10,27–31].

The NMR properties of a series of organophosphorus compounds **3, 4**, and **8** are listed in Table 3. The relative trends in the chemical shifts of **3, 4**, and **8** are consistent and independent of the substituents on the oxygen atom in ^{31}P NMR spectra. Among these, the signals of **3** were observed in the highest regions, whereas those of **4** were in the lowest regions. The signals of **8** were midway between those of **3** and **4**. All of the signals in the ^{19}F

TABLE 3 NMR Spectra of a Series of Organophosphorus Compounds **3, 4**, and **8**

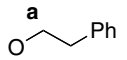
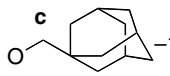
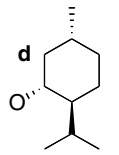
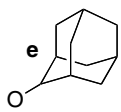
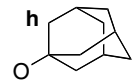
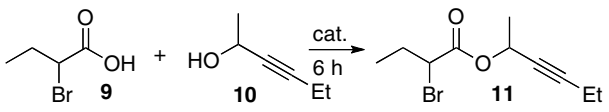
OR	PhO, PhO **3** OR			Bu4N+ -O, F **4** OR			HO, F **8** OR		
	^{31}P (δ)	^{31}P (δ)	^{19}F (δ)	$^{1}J_{P\text{-}F}$ (Hz)	^{31}P (δ)	^{19}F (δ)	$^{1}J_{P\text{-}F}$ (Hz)
a 	−11.5	−4.7	−77.5	923.6	−7.7	−80.6	950.0
c 	−11.0	−3.6	−79.0	918.0	−6.6	−81.3	945.4
d 	−11.9	−5.4	−74.7	919.5	−7.8	−77.5	945.4
e 	−12.0	−4.7	−73.6	918.3	−8.6	−77.8	945.4
h 	−16.4	−8.3	−67.0	919.7	−10.1	−71.4	944.3

TABLE 4 Reaction of 2-Bromobutanoic Acid (**9**) with 3-Hexyne-2-ol (**10**) in the Presence of Acid Catalysts[a]



Entry	*Acid Catalyst*	*Temperature*	**9**	**10**	**11**
1	H_2SO_4	140°C	1	0	0
2	TsOH	140°C	1	0	0
3	**8a**	140°C	1.2	0.55	1
4	**8c**	140°C	1	0.78	1
5	**8d**	140°C	0	0.10	1 (70%)[b]
6	**8e**	100°C	3.3	2.9	1
7	**8e**	120°C	2	2.7	1
8	**8e**	140°C	0.89	0.67	1
9	**8h**	140°C	1	0.45	1

[a] Relative ratios of **9** **10**, and **11** as determined by ^{1}H NMR spectra.
[b] Isolated yield.

NMR spectra were observed at −67 to −81 ppm and the protonation of **4** slightly shifted the signals to a higher region by 2.3–4.1 ppm. In all cases, the 1-adamantyl group affected the signals of **3h, 4h**, and **8h**, which slightly differed from the mean values of other derivatives. In contrast, the 1-adamantyl group had no effect on the ^1J coupling constants between phosphorus and fluorine atoms. The coupling constants of **8** were greater than those of **4** by around 27 Hz.

Finally, the catalytic activities of acids **8** in the condensation reaction between acid **9** and propargyl alcohol **10** were tested under solvent-free conditions [32] because the development of reactions under solvent-free conditions is an important subject in synthetic chemistry [33]. The results are shown in Table 4. The reaction of **9** and **10** in the presence of a catalytic amount of H_2SO_4 or TsOH at 140°C did not give the desired product **11** (entries 1 and 2). This result is probably due to the fact that these acids predominantly mediate dehydration of the alcohol **10** to mainly give the enyne. Phosphorofluoridic acids **8** were then used as an acid catalyst. Phosphorofluoridic acids **8** catalyzed the condensation regardless of the substituents attached to the oxygen atom of **8**, but the efficiency of the reaction highly depended on the substituents. On the basis of relative ratio of **9, 10**, and **11**, acids **8a** and **8h** facilitate the dehydration of **10** (entries 3 and 9), whereas acids **8c** and **8e** that were derived from secondary alcohols appear to catalyze both condensation and dehydration (entries 4 and 8). Notably, in the acid **8d**-catalyzed reaction, the starting acid **9** was completely consumed and the product **11** was the major component of the reaction mixture (entry 5). The reaction mixture was then purified by column chromatography on silica gel to give the ester **11** in 70% isolated yield.

CONCLUSION

The fluorinative hydrolysis of phosphoric acid alkyl diphenyl esters was demonstrated. The reaction took 7–20 h, but the starting esters were selectively converted to the corresponding phosphorofluoridic acid salt monoesters. Acid hydrolysis of the salts was achieved by treating the salts with Amberlyst 15. The NMR properties of a series of organophosphorus compounds were presented. Finally, the catalytic activities of phosphorofluoridic acids were examined in the condensation reaction of α-bromobutanoic acid and 3-hexyne-2-ol, and were found to depend on the structure of the alkyl groups in the acid catalysts.

EXPERIMENTAL

Typical Procedure for the Synthesis of Phosphoric Acid Alkyl Diphenyl Esters

*Synthesis of Phosphoric Acid 1-tricyclo [3.3.1.13,7]dec Diphenyl Ester (***3h***).* To a CH_2Cl_2 solution (20 mL) of diphenylphosphoryl chloride (**1**) (2.1 mL, 10 mmol), 1-adamantanol (1.5 g, 10 mmol) and DMAP (2.4 g, 20 mmol) were added under an Ar atmosphere. The resulting solution was stirred at room temperature for 5 h and concentrated in vacuo. The reaction mixture was purified by column chromatography on silica gel (EtOAc : hexane = 1:3, Rf = 0.45) to give the corresponding ester **3h** (3.31 g, 86%) as a colorless oil.

IR (neat): 3069, 2913, 2854, 2684, 1942, 1738, 1592, 1490, 1456, 1371, 1357, 1592, 1490, 1456, 1371, 1357, 1284, 1224, 1191, 1163, 1105, 1051, 1018, 945, 903, 849, 814, 775, 712, 689, 642, 617, 587, 558, 525, 515, 506, 488, 478, 459, 445, 433, 420, 411, 402 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.58–1.69 (m, 6H, $OCCH_2CHC\underline{H}_2$), 2.09–2.17 (m, 6H, $OCC\underline{H}_2$), 4.04–4.20 (m, 3H, $OCCH_2C\underline{H}$), 7.14–7.35 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$): δ 31.2 ($OCCH_2\underline{C}H$), 35.5 ($OCCH_2CH\underline{C}H_2$), 43.3 (d, $^3J_{C\text{-}P}$ = 4.1 Hz, $OC\underline{C}H_2$), 85.1 (d, $^2J_{C\text{-}P}$ = 8.3 Hz, $O\underline{C}CH_2$), 120.0, 120.1, 124.9, 129.5, 150.8, 150.9 (Ph); ^{31}P NMR ($CDCl_3$): δ −16.4; MS (EI) 384 *m/z* (M^+); HRMS Calcd. for $C_{22}H_{25}O_4P$ (M^+): 384.1490. Found: 384.1480.

*Phosphoric Acid 2-Naphthylethyl Diphenyl Ester (**3b**)*. Colorless solid; mp: 62–63°C; IR(KBr): 3100, 3051, 3015, 2955, 2929, 2892, 2414, 2318, 1959, 1930, 1876, 1811, 1739, 1589, 1488, 1456, 1392, 1365, 1312, 1272, 1233, 1192, 1166, 1070, 1023, 1023, 960, 905, 870, 822, 762, 689, 648, 616, 576, 545, 536, 503, 466, 411 cm^{-1}; ^1H NMR ($CDCl_3$): δ3.17 (t, $J = 6.8$ Hz, 2H, $OCH_2C\underline{H}_2$), 4.53 (dt, $J = 6.9$ Hz, 6.9 Hz, 2H, $OC\underline{H}_2$), 7.10–7.82 (m, 17H, Ar); ^{13}C NMR ($CDCl_3$): δ 36.8 (d, $^3J_{C\text{-}P} = 7.0$ Hz, $OCH_2\underline{C}H_2$), 69.4 (d, $^2J_{C\text{-}P} = 6.6$ Hz, $O\underline{C}H_2$), 119.99, 120.04, 125.3, 125.7, 126.1, 127.2, 127.6, 127.65, 127.71, 128.3, 129.7, 132.4, 133.5, 134.2, 150.4, 150.5 (Ar); ^{31}P NMR ($CDCl_3$): δ −11.8; MS (EI) *m/z* 404 (M^+); HRMS Calcd. for $C_{24}H_{21}O_4P$: 404.1177. Found: 404.1160.

*Phosphoric Acid Tricyclo[3.3.1.13,7]dec-1-methyl Diphenyl Ester (**3c**)*. Colorless oil; IR (neat): 3904, 3868, 3841, 3674, 3631, 3495, 3070, 2892, 2754, 2678, 2659, 2575, 2409, 1939, 1784, 1737, 1593, 1494, 1453, 1388, 1365, 1345, 1294, 1193, 1108, 942, 905, 863, 808, 768, 754, 689, 661, 617, 606, 578, 567, 538, 502, 486, 450, 437, 414, 400 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.47–1.57 (m, 6H, $OCH_2CCH_2CHC\underline{H}_2$), 1.66 (d, $J = 28.8$ Hz, 3H, $CC\underline{H}_2CHCH_2$ and d, $J = 52.7$ Hz, 3H, $CC\underline{H}_2CHCH_2$), 1.85–2.04 (m, 3H, $CCH_2C\underline{H}$), 3.81 (d, $J = 5.4$ Hz, 2H, $OC\underline{H}_2CCH_2$), 7.14–7.42 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$): δ 27.8 ($OCH_2CCH_2\underline{C}H$), 34.0 ($OCH_2\underline{C}CH_2$), 36.8 ($OCH_2CCH_2CH\underline{C}H_2$), 38.6 ($OCH_2C\underline{C}H_2CH$), 78.6 (d, $^2J_{C\text{-}P} = 7.4$ Hz, $O\underline{C}H_2CCH_2$), 120.1, 125.2, 129.7, 150.6 (Ph); ^{31}P NMR ($CDCl_3$): δ −11.0; MS (EI) *m/z* 398 (M^+); HRMS Calcd. for $C_{23}H_{27}O_4P$ (M^+): 398.1647. Found: 398.1651.

*Phosphoric Acid l-Menthyl Diphenyl Ester (**3d**)*. IR(neat): 3070, 3044, 2955, 2870, 2366, 1941, 1720, 1592, 1490, 1456, 1388, 1370, 1349, 1289, 1223, 1193, 1163, 1110, 1061, 1016, 947, 903, 882, 829, 807, 774, 689, 617, 589, 546, 526, 511, 448, 432, 410 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.73 (d, $J = 6.8$ Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.86 (d, $J = 6.8$ Hz, 3H, $OCHCHCH[C\underline{H}_3)_2]$, 0.90 [d, $J = 6.8$ Hz, 3H, $OCHCHCH(C\underline{H}_3)_2]$, 0.80–1.06 (m, 2H), 1.19 (q, $J = 11.7$ Hz, 1H), 1.38–1.46 (m, 2H), 1.66 (br d, $J = 11.2$ Hz, 2H), 1.99–2.06 [m, 1H, $C\underline{H}(CH_3)_2$], 2.23 (br d, $J = 12.2$ Hz, 1H), 4.43 (ddt, $J = 11.2$ Hz, 6.8 Hz, 4.4 Hz, 1H, $OC\underline{H}$), 7.15–7.36 (m, 10H, Ph); ^{31}P NMR ($CDCl_3$): δ −11.9; MS (EI) *m/z* 388 (M^+); HRMS Calcd. for $C_{22}H_{29}O_4P$: 388.1803. Found: 388.1789.

*Phosphoric Acid 2-Adamantyl Diphenyl Ester (**3e**)*. Colorless solid; mp: 58°C–59°C; IR(KBr): 3097, 3067, 3042, 3015, 2899, 2854, 2679, 2637, 2431, 2398, 2374, 2331, 2265, 2232, 2140, 1983, 1955, 1924, 1866, 1790, 1727, 1685, 1591, 1492, 1452, 1385, 1366, 1358, 1344, 1280, 1193, 1114, 1102, 1068, 1043, 869, 830, 817, 772, 739, 688, 637, 616, 586, 543, 521, 511, 500, 456, 445, 418 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.50–1.53 (m, 2H), 1.71–1.73 (m, 4H), 1.81–1.86 (m, 4H), 2.02–2.05 (m, 2H), 2.10 (br, 2H), 4.79–4.82 (m, 1H, $OC\underline{H}$), 7.15–7.35 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$): δ 26.7, 27.1, 31.1, 33.3 (d, $J = 4.1$ Hz), 36.3, 37.3, 84.0 (d, $^2J_{C\text{-}P} = 7.4$ Hz, $O\underline{C}H$), 120.2 (d, $J = 5.0$ Hz), 125.1, 129.7, 150.9 (d, $J = 5.8$ Hz) (Ph); ^{31}P NMR ($CDCl_3$): δ −12.0; MS (EI): *m/z*: 384 (M^+); HRMS Calcd. for $C_{22}H_{25}O_4P$: 384.1490. Found: 384.1498.

*Phosphoric Acid 1,4:3,6-Dianhydro-5-O-benzylglucide Diphenyl Ester (**3f**)*. Colorless oil; IR (neat): 3919, 3887, 3862, 3823, 3761, 3737, 3691, 3649, 2925, 1590, 1488, 1456, 1286, 1189, 1163, 1024, 953, 756, 688, 616, 573, 560, 520, 499, 486, 476, 463, 444, 431, 409 cm^{-1};^1H NMR ($CDCl_3$): δ 3.62 (t, $J = 8.0$ Hz, 1H), 3.88 (m, 1H), 4.04–4.20 (m, 3H), 4.56–4.60 (m, 2H), 4.70–4.72 (m, 1H, $POC\underline{H}$), 4.78 (d, $J = 12.2$ Hz, 1H), 5.06–5.08 (m, 1H), 7.01–7.38 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$): δ 70.4, 72.5, 74.0 (d, $J = 4.1$ Hz), 79.0, 80.5, 82.7 (d, $J = 6.6$ Hz), 86.2 (d, $J = 6.6$ Hz), 120.0, 125.5, 127.9, 128.0, 128.5, 129.8, 137.5, 150.2, 150.3; ^{31}P NMR ($CDCl_3$): δ −12.5; MS (EI) *m/z* 468 (M^+); HRMS Calcd. for 468.1357.

*Phosphoric Acid 1,4:3,6-Dianhydro-2-O-benzylglucide Diphenyl Ester (**3g**)*. Colorless oil; IR (neat): 3435, 3066, 2925, 2873, 1951, 1735, 1685, 1590, 1490, 1456, 1372, 1293, 1220, 1190, 1164, 1071, 1026, 955, 833, 773, 690, 634, 617, 577, 517, 479, 469, 461, 452, 438, 424, 415, 403 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.71 (dd, $J = 6.3$ Hz, 1H), 3.82–3,88 (m, 2H), 3.97–4.11 (m, 2H), 4.49–4.55 (m, 3H), 4.72–4.74 (m, 1H), 4.95–5.01 (m, 1H, $POC\underline{H}$), 7.13–7.29 (m, 15H, Ph);^{13}C NMR ($CDCl_3$): δ 70.1 (d, $J = 6.6$ Hz), 71.4, 73.5, 78.1 (d, $J = 5.8$ Hz), 80.6 (d, $J = 4.1$ Hz), 83.2, 86.1, 120.1, 125.4, 127.7, 127.9, 128.5, 129.7, 137.4, 150.3; ^{31}P NMR ($CDCl_3$): δ −11.6; MS (EI) *m/z* 468 (M^+); HRMS Calcd. for $C_{25}H_{25}O_7P$ (M^+): 468.1338. Found 468.1324.

Typical Procedure for Fluorinative Hydrolysis of Alkyl Diphenyl Phosphoric Acid Esters

*Synthesis of N,N,N-Tributyl-1-butanaminium 2-Phenylethylphosphorofluoridate (**4a**)*. To a THF solution (8 mL) of ester **3a** (709 mg, 2.0 mmol), tetrabutylammonium fluoride (1.0 M, THF) (4.0 mL, 4.0 mmol) was added at room temperature under an Ar atmosphere. The mixture was stirred for 16 h at room temperature. The reaction mixture was poured

into water and extracted with Et_2O (40 mL). The organic layer was washed with water (40 mL × 2). The water layer was extracted with CH_2Cl_2 (120 mL × 3) and 15% aqueous sodium hydroxide (20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to give an ammonium salt **4a** (861 mg, 97%) as a colorless solid; mp: 101–102°C° IR (KBr): 3626, 3594, 3567, 3478, 3446, 3393, 3331, 3313, 3263, 2874, 2365, 1644, 1488, 1281, 1118, 1034, 885, 798, 763, 747, 699, 669, 638, 593, 578, 563, 535, 503, 495, 482, 461, 450, 440, 427, 408 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.98 (t, J = 7.3 Hz, 12H, $C\underline{H}_3$), 1.42 (sext, J = 7.3 Hz, 8H, $C\underline{H}_2CH_3$), 1.58–1.62 (m, 8H, $NCH_2C\underline{H}_2$), 2.98 (t, J = 7.3 Hz, 2H, $OCH_2C\underline{H}_2Ph$), 3.27 (t, J = 8.3 Hz, 8H, $NC\underline{H}_2CH_2$), 4.15 (q, J = 7.8 Hz, 2H, $OC\underline{H}_2CH_2Ph$), 7.03–7.25 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$): δ 13.6 ($\underline{C}H_3$), 19.7 ($\underline{C}H_2CH_3$), 24.0 ($NCH_2\underline{C}H_2$), 37.3 (d, $^3J_{C\text{-}P}$ = 6.6Hz, $OCH_2\underline{C}H_2Ph$), 58.7 ($N\underline{C}H_2$), 66.5 (d, $^2J_{C\text{-}P}$ = 6.6Hz, $O\underline{C}H_2CH_2Ph$), 125.9, 128.1, 129.0, 138.8 (Ph); ^{31}P NMR ($CDCl_3$): δ −4.71 (d, $^1J_{P\text{-}F}$ = 923.6 Hz); ^{19}F NMR ($CDCl_3$): δ −77.5 (d, $^1J_{P\text{-}F}$ = 923.5 Hz); MS (FAB) m/z 203 (M^+—Bu_4N).

N,N,N-Tributyl-1-butanaminium 2-(2-Naphthyl) ethylphosphorofluoridate (**4b**). Colorless liquid; IR (neat): 3052, 2962, 2875, 2193, 1632, 1601, 1508, 1469, 1382, 1113, 1067, 1038, 931, 887, 856, 819, 784, 731, 640, 533, 498, 478 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.98 (t, J = 7.4 Hz, 12H, $CH_2C\underline{H}_3$), 1.40 (sex, J = 7.4 Hz, 8H, $C\underline{H}_2CH_3$), 1.55–1.63 (m, 8H, $C\underline{H}_2CH_2CH_3$), 3.15 (t, J = 7.4 Hz, 2H, $OCH_2C\underline{H}_2$), 3.20–3.25 (m, 8H, $NC\underline{H}_2$), 4.27 (dt, J = 7.6 Hz, 7.5 Hz, 2H, $OC\underline{H}_2$), 7.38–7.79 (m, 7H, Ar); ^{13}C NMR ($CDCl_3$): δ 13.7 ($CH_2\underline{C}H_3$), 19.7 ($\underline{C}H_2CH_3$), 24.0 ($\underline{C}H_2CH_2CH_3$), 37.4 (d, $^3J_{C\text{-}P}$ = 6.8 Hz, $OCH_2\underline{C}H_2$), 58.8 ($N\underline{C}H_2$), 66.5 (d, $^2J_{C\text{-}P}$ = 5.4 Hz, $O\underline{C}H_2$), 125.1, 125.7, 127.3, 127.6, 127.7, 127.9, 132.1, 133.6, 136.5 (Ar); ^{19}F NMR ($CDCl_3$): δ −78.0 (d, $^1J_{P\text{-}F}$ = 923.2 Hz); ^{31}P NMR ($CDCl_3$): δ −5.0 (d, $^1J_{P\text{-}F}$ = 923.2 Hz); Anal Calcd. for $C_{28}H_{47}FO_3P{\cdot}1H_2O$ (495.3278): C, 65.52; H, 9.51; N, 2.87. Found: C, 65.47; H, 9.62; N, 2.73.

N,N,N-Tributyl-1-butanaminium Tricyclo [3.3.1.13,7] dec-1-methyl Phosphorofluoridate (**4c**). Colorless solid; mp: 155–156°C° IR (neat): 3902, 3842, 3798, 3729, 3674, 3439, 2905, 2849, 2676, 1638, 1593, 1490, 1465, 1383, 1363, 1345, 1273, 1189, 1156, 1112, 1047, 989, 941, 921, 884, 849, 806, 772, 693, 608, 577, 521, 499, 480, 468, 444, 427, 409 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.00 (t, J = 7.3 Hz, 12H, $C\underline{H}_3$), 1.45 (sext, J = 7.3 Hz, 8H, $C\underline{H}_2CH_3$), 1.51–1.57 (m, 6H, $OCH_2CCH_2CHC\underline{H}_2$), 1.61–1.74 (m, 8H, $NCH_2C\underline{H}_2$ and m, 6H, $CC\underline{H}_2CHCH_2$), 1.86–1.94 (dr, 3H, $CCH_2C\underline{H}CH_2$), 3.33 (t, J = 8.3 Hz, 8H, $NC\underline{H}_2CH_2$), 3.54 (d, J = 5.4 Hz, 2H, $OC\underline{H}_2CCH_2$); ^{13}C NMR ($CDCl_3$): δ 13.7 ($\underline{C}H_3$), 19.7 ($\underline{C}H_2CH_3$), 24.0 ($\underline{C}H_2CH_2CH_3$), 28.2 ($OCH_2CCH_2\underline{C}H$), 33.8 (d, $^3J_{C\text{-}P}$ = 8.3 Hz, $OCH_2\underline{C}CH_2$), 37.2 ($OCH_2CCH_2CH\underline{C}H_2$), 39.0 ($OCH_2C\underline{C}H_2CH$), 58.7 ($N\underline{C}H_2$), 76.0 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, $O\underline{C}H_2CCH_2$); ^{31}P NMR ($CDCl_3$): δ −3.64 (d, $^1J_{P\text{-}F}$ = 917.7 Hz); ^{19}F NMR ($CDCl_3$): δ −79.0 (d, $^1J_{P\text{-}F}$ = 918.2 Hz); MS (FAB) m/z 247 (M^+—Bu_4N).

N,N,N-Tributyl-1-butanaminium L-Menthyl Phosphorofluoridate (**4d**). Colorless solid; mp: 48–49°C; IR (KBr): 2967, 2872, 2733, 2360, 2341, 1645, 1487, 1383, 1281, 1179, 1151, 1094, 1078, 1060, 1028, 1000, 931, 884, 825, 807, 750, 552, 520, 495, 453, 413 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.70–0.77 (m, 1H), 0.74 (d, J = 7.2 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.79 (d, J = 6.8 Hz, 3H, $OCHCHCH(C\underline{H}_3)_2$), 0.80 (d, J = 7.2 Hz, 3H, $OCHCHCH(C\underline{H}_3)_2$), 0.86–1.02 (m, 1H), 0.94 (t, J = 7.4 Hz, 12H, $CH_2C\underline{H}_3$), 1.16–1.23 (m, 1H), 1.38 (sex, J = 7.3 Hz, 8H, $C\underline{H}_2CH_3$), 1.33–1.63 (m, 4H, $C\underline{H}_2$ and/or $C\underline{H}$), 1.53–1.63 (m, 8H, $C\underline{H}_2CH_2CH_3$), 2.25–2.28 (m, 2H), 3.24–3.28 (m, 8H, $NC\underline{H}_2$), 3.93–4.01 (m, 1H, $OC\underline{H}$); ^{13}C NMR ($CDCl_3$): δ 13.6 ($CH_2\underline{C}H_3$), 15.8, 19.6 ($\underline{C}H_2CH_3$), 21.2, 22.1, 22.9, 23.9 ($\underline{C}H_2CH_2CH_3$), 25.2, 31.4, 34.5, 43.0, 48.8 (d,J = 7.2 Hz), 58.6 ($N\underline{C}H_2$), 75.7 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, $O\underline{C}H$); ^{19}F NMR ($CDCl_3$): δ −74.7 (d, $^1J_{P\text{-}F}$ = 919.5 Hz); ^{31}P NMR ($CDCl_3$): δ −5.4 (d, $^1J_{P\text{-}F}$ = 919.5 Hz); MS (FAB^-): m/z: 237 (M^-); Anal Calcd for $C_{26}H_{55}FO_3P{\cdot}0.5H_2O$ (479.3904): C, 63.62; H, 11.71; N, 2.74. Found: C, 63.90; H, 11.55; N, 2.87.

N,N,N-Tributyl-1-butanaminium 2-Tricyclo [3.3.1.13,7]decphosphorofluoridate (**4e**). Colorless solid; mp: 151–153°C; IR (KBr): 2979, 2672, 1456, 1382, 1272, 1120, 1080, 1056, 981, 954, 861, 814, 777, 670, 639, 619, 544, 503, 449, 405 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.97 (t, J = 7.3 Hz, 12H, $CH_2C\underline{H}_3$), 1.42 (sex, J = 7.3 Hz, 8H, $C\underline{H}_2CH_3$), 1.58–1.65 (m, 8H, $NCH_2C\underline{H}_2$), 1.65–1.73 (m, 10H), 2.08 (br, 2H), 2.19–2.22 (m, 2H), 4.38–4.42 (m, 1H, $OC\underline{H}$); ^{13}C NMR ($CDCl_3$): δ 13.6 ($CH_2\underline{C}H_3$), 19.7 ($\underline{C}H_2CH_3$), 24.0 ($NCH_2\underline{C}H_2$), 27.2, 27.5, 31.3, 33.3 (d, J = 4.9 Hz), 36.5, 37.8, 78.5 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, $O\underline{C}H$); ^{19}F NMR ($CDCl_3$): δ −73.6 (d, $^1J_{P\text{-}F}$ = 918.3 Hz); ^{31}P NMR ($CDCl_3$): δ −4.7 (d, $^1J_{P\text{-}F}$ = 918.3 Hz); MS (FAB^-): m/z: 233 (M^-).

N,N,N-Tributyl-1-butanaminium 1,4:3,6-Dianhydro-2-O-benzylglucidephosphorofluoridate (**4f**). Colorless oil; $[\alpha]_D^{25}$ = +24.0 (c = 1.0, $CHCl_3$); IR (neat): 3410, 2960, 2873, 1648, 1458, 1383, 1291, 1208, 1093, 1017, 979, 933, 887, 855, 829, 776, 739, 700, 611, 538, 500, 478, 466, 454, 429, 415 cm^{-1}; ^1H

NMR ($CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 12H, $C\underline{H}_3$), 1.35 (sext, J = 7.3 Hz, 8H, $C\underline{H}_2CH_3$), 1.52–1.56 (m, 8H, $NCH_2C\underline{H}_2$), 3.22 (t, J = 8.3 Hz, 8H, $NC\underline{H}_2CH_2$), 3.62–3.70 (m, 1H), 3.88 (d, J = 2.9 Hz, 2H), 3.94–3.99 (m, 2H), 4.44–4.52 (m, 3H), 4.58–4.60 (m, 1H), 4.71–4.81 (m, 1H, POC$\underline{H}$), 7.16–7.29 (m, 5H, Ph);^{13}C NMR ($CDCl_3$): δ 13.7 ($\underline{C}H_3$), 19.7 ($\underline{C}H_2CH_3$), 24.0 ($NCH_2\underline{C}H_2$), 58.7 ($N\underline{C}H_2$), 69.8 (d, J = 5.8 Hz), 71.4, 73.3, 75.4 (d, J = 5.8), 81.2 (d, J = 5.0 Hz), 84.1, 85.5, 127.6, 127.7, 128.4, 137.7 (Ph); ^{31}P NMR ($CDCl_3$): δ −5.90 (d, $^1J_{P\text{-}F}$ = 929.6 Hz); ^{19}F NMR ($CDCl_3$): δ −75.6 (d, $^1J_{P\text{-}F}$ = 931.1 Hz); MS (FAB) *m/z* 317 (M^+—Bu_4N).

*N,N,N-Tributyl-1-butanaminium 1,4:3,6-Dianhydro-2-O-benzylglucidephosphorofluoridate (***4g***).* Colorless oil; $[\alpha]_D^{25}$ = +54.1 (c = 1.0, $CHCl_3$); IR (neat): 3402, 2962, 2875, 1647, 1465, 1382, 1280, 1119, 1078, 1007, 886, 822, 745, 701, 604, 511, 472, 460, 443, 433, 422, 409 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.97 (t, J = 7.3 Hz, 12H, $C\underline{H}_3$), 1.41 (sext, J = 7.4 Hz, 8H, $C\underline{H}_2CH_3$), 1.58–1.62 (m, 8H, $NCH_2C\underline{H}_2$), 3.26 (t, J = 8.3 Hz, 8H, $NC\underline{H}_2CH_2$), 3.53 (t, J = 8.3 Hz, 1H), 3.82 (t, J = 7.8 Hz, 1H), 3.94–4.04 (m, 2H), 4.13–4.19 (m, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.58–4.62 (m, 1H), 4.62–4.66 (m, 1H), 4.72 (d, J = 11.7 Hz, 1H), 4.76–4.81 (m, 1H), 7.24–7.32 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$): δ 13.6 ($\underline{C}H_3$), 19.7 ($\underline{C}H_2CH_3$), 24.0 ($NCH_2\underline{C}H_2$), 58.7 ($N\underline{C}H_2$), 69.6, 72.3, 75.1 (d, J = 4.1 Hz), 79.5, 79.9, 80.0 (d, J = 3.0 Hz), 87.2 (d, J = 7.4 Hz), 127.8, 128.0, 128.4, 129.2, 137.8 (Ph); ^{31}P NMR ($CDCl_3$): δ −6.58 (d, J = 926.6 Hz); ^{19}F NMR ($CDCl_3$): δ −74.7 (d, $^2J_{P\text{-}F}$ = 928.1 Hz); MS (FAB) *m/z* 317 (M^+—Bu_4N).

*N,N,N-Tributyl-1-butanaminium 1-Tricyclo [3.3.1.13,7]decphosphorofluoridate (***4h***).* Viscous solid; IR (neat): 3925, 3903, 3882, 3856, 3845, 3755, 3738, 3693, 3679, 3402, 2912, 2681, 2343, 1637, 1604, 1592, 1489, 1458, 1382, 1368, 1357, 1260, 1184, 1151, 1119, 1101, 1067, 1029, 998, 984, 961, 934, 885, 838, 813, 773, 711, 695, 643, 618, 592, 542, 508, 479, 467, 454, 441, 419 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.00 (t, J = 7.3 Hz, 12H, $C\underline{H}_3$), 1.45 (sext, J = 7.8 Hz, 8H, $C\underline{H}_2CH_3$), 1.54–1.71 (m, 8H, $NCH_2C\underline{H}_2$, m, 6H, $OCCH_2CHC\underline{H}_2$), 2.05–2.15 (m, 6H, $OCC\underline{H}_2$), 2.15–2.24 (m, 3H, $OCCH_2C\underline{H}$), 3.32 (t, J = 8.3 Hz, 8H, $NC\underline{H}_2CH_2$); ^{13}C NMR ($CDCl_3$): δ 13.7 ($\underline{C}H_3$), 19.7 ($\underline{C}H_2CH_3$), 24.0 ($\underline{C}H_2CH_2CH_3$), 31.0 ($OCCH_2\underline{C}H$), 36.2 ($OCCH_2CH\underline{C}H_2$), 43.3 (d, $^3J_{C\text{-}P}$ = 4.1 Hz, $OC\underline{C}H_2$), 58.8 ($N\underline{C}H_2$), 68.0 ($O\underline{C}CH_2$); ^{31}P NMR ($CDCl_3$): δ −8.27 (d, $^1J_{P\text{-}F}$ = 920.7 Hz); ^{19}F NMR ($CDCl_3$): δ −67.0 (d, $^1J_{P\text{-}F}$ = 919.7 Hz); MS (FAB) *m/z* 233 (M^+—Bu_4N).

Typical Procedure for Methylation of the Salts: Synthesis of a Mixture of Diastereomers of Phosphorofluoridic Acid and l*-Menthyl Methyl Ester (***7d***)*

To an Et_2O solution (3 mL) of the ammonium salt **4d** (170 mg, 0.35 mmol), iodomethane (89 μL, 1.4 mmol) was added under an Ar atmosphere. After the addition was complete, the mixture was stirred for 4 h at room temperature. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo, and purified by column chromatography on silica gel (ethyl acetate: hexane = 1:3, Rf = 0.53) to give to give diastereomeric mixture (51:49) **7d** (21 mg, 24%) as a colorless oil. IR (neat): 2958, 2872, 1458, 1304, 1025, 878, 788, 430, 418 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.75 (d, J = 6.8 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.76 (d, J = 7.2 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.86 (d, J = 6.8 Hz, 6H, $OCHCHCH(C\underline{H}_3)_2$), 0.87 (d, J = 6.0 Hz, 6H, $OCHCHCH(C\underline{H}_3)_2$), 0.78–1.01 (m, 2H, m, 2H), 1.01–1.20 (m, 1H, m, 1H), 1.31–1.42 (m, 2H, m, 2H), 1.60–1.63 (m, 2H, m, 2H), 2.00–2.04 (m, 1H, m, 1H), 2.12–2.16 (m, 1H, m, 1H), 3.81 (d, J = 11.2 Hz, 3H, $OC\underline{H}_3$), 3.82 (d, J = 11.6 Hz, 3H, $OC\underline{H}_3$), 4.22–4.31 (m, 1H, $OC\underline{H}$, m, 1H, $OC\underline{H}$); ^{13}C NMR ($CDCl_3$): δ 15.6, 15.7, 20.8, 20.8, 21.9, 21.9, 23.0, 23.0, 25.7, 25.8, 31.5, 31.5, 33.8, 33.8, 42.2, 42.3, 48.2, 48.3, 55.2 (d, J = 6.6 Hz, $O\underline{C}H_3$), 55.3 (d, J = 5.8 Hz, $O\underline{C}H_3$), 82.08 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, $O\underline{C}H$), 82.14 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, $O\underline{C}H$); ^{19}F NMR ($CDCl_3$): δ −79.6 (d, $^1J_{P\text{-}F}$ = 976.9 Hz), −81.8 (d, $^1J_{P\text{-}F}$ = 976.9 Hz); ^{31}P NMR ($CDCl_3$): δ −7.7 (d, $^1J_{P\text{-}F}$ = 976.9 Hz), −8.1 (d, $^1J_{P\text{-}F}$ = 976.9 Hz).

*Phosphorofluoridic Acid Methyl 2-Naphthylethyl Ester (***7b***).* IR (neat): 3402, 2960, 1602, 1509, 1458, 1313, 1192, 1115, 1029, 948, 887, 822, 749, 619, 521, 481, 411, 402 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.10 (t, J = 6.8 Hz, 2H, $OCH_2C\underline{H}_2$), 4.32 (dt, J = 7.8 Hz, 7.3 Hz, 2H, $OC\underline{H}_2$), 7.12–7.77 (m, 7H, Ar); ^{13}C NMR ($CDCl_3$): δ 39.0 (d, J = 6.6 Hz, $OCH_2\underline{C}H_2$), 78.2 (dd, J = 1.7 Hz, J = 1.7 Hz, $O\underline{C}H_2$), 126.1, 128.4, 128.5, 141.1 (Ar); ^{19}F NMR ($CDCl_3$): δ −77.8 (d, $^1J_{P\text{-}F}$ = 945.8 Hz); ^{31}P NMR ($CDCl_3$): δ −8.4 (d, $^1J_{P\text{-}F}$ = 945.8 Hz); MS (EI): *m/z*: 268 (M^+); HRMS Calcd for $C_{13}H_{14}FO_3P$: 268.0659, Found: 268.0640.

Typical Procedure for the Acid Hydrolysis of Phosphorofluoridic Acid Salt Monoesters

*Synthesis Phosphorofluoridic Acid 2-Phenylethyl Ester (***8a***).* To a CH_2Cl_2 solution (7 mL) of tetrabutylammonium salt **4a** (446 mg, 1.0 mmol), Amberlyst15 H^+ (2.92 g) was added at room

temperature. The mixture was stirred for 2 h at room temperature. The reaction mixture was filtered and washed with CH_2Cl_2 (10 mL). The filtrate was dried over $MgSO_4$, filtered, and concentrated in vacuo to give phosphorofluoridic acid **8a** (186 mg, 91%) as a colorless oil. IR (neat): 3031, 2967, 1698, 1497, 1472, 1455, 1217, 1057, 903, 749, 700, 590, 576, 527, 494, 439, 427, 417, 401 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.10 (1H, PO$\underline{H}$), 2.96 (t, J = 7.1 Hz, 2H, C$\underline{H}_2$CH_2O), 4.26 (q, J = 7.3 Hz, 2H, CH_2C$\underline{H}_2$O), 7.10–7.26 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$): δ 36.4 (d, $^3J_{C\text{-}P}$ = 7.4 Hz, OCH_2C$\underline{H}_2$Ph), 69.8 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, OC$\underline{H}_2$CH_2Ph), 127.0, 128.6, 128.9, 136.1 (Ph); ^{31}P NMR ($CDCl_3$): δ −7.66 (d, $^1J_{P\text{-}F}$ = 950.3 Hz); ^{19}F NMR ($CDCl_3$): δ −80.6 (d, $^1J_{P\text{-}F$ = 949.4 Hz); MS (EI) *m/z* 204 (M^+); HRMS Calcd for $C_8H_{10}FO_3P$-H^+ (M^+) 203.0273, Found 203.0284.

*Phosphofluoridic Acid Tricyclo[3.3.1.13,7]dec-1-methyl Ester (***8c***).* Viscous colorless solid; IR (neat): 2906, 2850, 2678, 2305, 1698, 1453, 1390, 1365, 1345, 1264, 1155, 1037, 945, 928, 893, 831, 803, 719, 648, 599, 504, 480, 468, 440, 428, 406 cm^{-1};^1H NMR ($CDCl_3$): δ 1.47–1.57 (m, 6H, OCH_2CCH_2CHC$\underline{H}_2$), 1.67 (d, J = 23.4 Hz, 3H, CC$\underline{H}_2$CHCH_2 and d, J = 47.3 Hz, 3H, CC$\underline{H}_2$CHCH_2), 1.95–2.05 (m, 3H, OCH_2CCH_2C$\underline{H}$), 3.70 (d, J = 5.8 Hz, 2H, OC$\underline{H}_2$CCH_2), 6.54 (s, 1H, PO$\underline{H}$);^{13}C NMR ($CDCl_3$): δ 27.8 (OCH_2CCH_2C$\underline{H}$), 34.0 (OCH_2C$\underline{C}$CH_2), 36.7 (OCH_2CCH_2C$\underline{H}$C$\underline{H}_2$), 38.4 (OCH_2C$\underline{C}$CH_2CH), 79.1 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, O$\underline{C}$CH_2CCH_2); ^{31}P NMR ($CDCl_3$: δ −6.58 (d, $^1J_{P\text{-}F}$ = 944.4 Hz); ^{19}F NMR ($CDCl_3$) δ −81.3 (d, $^1J_{P\text{-}F$ = 946.4 Hz); MS (EI) m/z 249 (M^+); HRMS Calcd for $C_{11}H_{18}FO_3P$-H^+ (M^+) 247.0899, Found 247.0877.

*Phosphorofluoridic Acid L-Menthyl Ester (***8d***).* Colorless oil; IR (neat): 3432, 2958, 2872, 2619, 2197, 1672, 1457, 1389, 1371, 1350, 1240, 1030, 978, 941, 902, 861, 819, 802, 595, 540, 511, 480, 451, 440, 402 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.79 (d, J = 6.8 Hz, 3H, OCHCH_2CHC$\underline{H}_3$), 0.90 (d, J = 7.4 Hz, 3H, OCHCHC(C$\underline{H}_3$)$_2$), 0.92 (d, J = 7.8 Hz, 3H, OCHCHC(C$\underline{H}_3$)$_2$), 0.78–1.05 (m, 3H), 1.22 (q, J = 11.9 Hz, 1H), 1.37–1.44 (m, 2H), 1.62–1.70 (m, 2H), 2.06–2.18 (m, 2H), 4.21–4.29 (m, 1H, OC$\underline{H}$); ^{13}C NMR ($CDCl_3$): δ 15.6, 20.8, 21.9, 23.0, 25.6, 31.6, 33.9, 42.1, 48.2 (d,J = 7.4 Hz), 82.1 (d, $^2J_{C\text{-}P}$ = 7.4 Hz, O$\underline{C}$H); ^{19}F NMR ($CDCl_3$): δ −77.5 (d, $^1J_{P\text{-}F$ = 945.4 Hz); ^{31}P NMR ($CDCl_3$): δ −7.8 (d, $^1J_{P\text{-}F$ = 945.4 Hz); MS (EI): *m/z*: 238 (M^+).

*Phosphorofluoridic Acid 2-Tricyclo[3.3.1.13,7] dec Ester (***8e***).* IR(neat): 3365, 2911, 2859, 2360, 1454, 1387, 1267, 1081, 1031, 960, 914, 890, 832, 672, 636, 526, 497, 446, 438, 426 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.52–1.55 (m, 2H), 1.68–1.71 (m, 4H), 1.81–1.88 (m, 4H), 2.07–2.10 (m, 4H), 4.60 (br, 1H, OC$\underline{H}$), 8.39 (br, 1H, O$\underline{H}$); ^{13}C NMR ($CDCl_3$): δ 26.6, 27.0, 30.9, 33.1 (d, J = 9.6 Hz), 36.2, 37.2, 84.5 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, O$\underline{C}$H); ^{19}F NMR ($CDCl_3$): δ −77.8 (d, $^1J_{P\text{-}F$ = 945.4 Hz); ^{31}P NMR ($CDCl_3$): δ −8.6 (d, $^1J_{P\text{-}F$ = 945.4 Hz); MS (EI) *m/z* 234 (M^+) HRMS. Calcd for $C_{10}H_{16}NO_3P$: 234.0821, Found: 234.0819.

*Phosphorofluoridic Acid 1-Tricyclo[3.3.1.13,7] dec Ester (***8h***).* Colorless oil; IR (neat): 3988, 3966, 3954, 3932, 3922, 3911, 3900, 3886, 3858, 3820, 3805, 3790, 3762, 3749, 3735, 3719, 3708, 3620, 3608, 3453, 3431, 3341, 2842, 2663, 1616, 1593, 1519, 1453, 1419, 1384, 1353, 1335, 1315, 1301, 1281, 1227, 1174, 1116, 1088, 1038, 1014, 982, 927, 891, 813, 776, 755, 723, 643 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.56–1.65 (m, 6H, OCCH_2CHC$\underline{H}_2$), 1.71 (d, J = 9.3 Hz, 6H, OCC$\underline{H}_2$), 2.10–2.15 (m, 3H, OCCH_2C$\underline{H}$), 3.20–3.22 (br, 1H, PO$\underline{H}$); ^{13}C NMR ($CDCl_3$): δ 30.7 (OCCH_2C$\underline{H}$), 35.5 (OCCH_2CHC$\underline{H}_2$), 36.0 (OC$\underline{C}$H$_2$), 45.2 (O$\underline{C}$CH$_2$); ^{31}P NMR ($CDCl_3$): δ −10.1 (d, $^1J_{P\text{-}F$ = 944.4 Hz); ^{19}F NMR ($CDCl_3$): δ −71.4 (d, $^1J_{P\text{-}F$ = 944.1 Hz); MS (EI) *m/z* 234 (M^+); HRMS Calcd. for $C_{10}H_{16}FO_3P$ (M^+) 234.0821. Found 234.0854.

*2-Methyl-3-hexyne 2-Bromobutyrate (***11***)*

Phosphoric acid *l*-menthyl ester **8e** (24 mg, 0.10 mmol), 2-bromobutyric acid (**9**) (0.21 mL, 2.0 mmol), and 3-hexyn-2-ol (**10**) (294 mg, 3.0 mmol) were added to a reaction tube. The resulting solution was stirred at 140°C° or 6 h. The reaction mixture was purified by column chromatography on silica gel (EtOAc : hexane = 1:10, Rf = 0.45) (column size: ϕ25 mm, height: *ca* 25 cm) to give the corresponding ester **11** (346 mg, 70%) as a colorless oil.

REFERENCES

[1] Dabkowski, W.; Tworowska, I. Org Biomol Chem 2005, 3, 866–874.
[2] Campion, C. L.; Li, W.; Lucht, B. L. J Electrochem Soc 2005, 152, A2327–A2334.
[3] Guranowski, A.; Wojdyla, A. M.; Zimny, J.; Wypijewska, A.; Kowalska, J.; Lukaszewicz, M.; Jemielity, J.; Darzynkiewicz, E.; Jagiello, A.; Bieganowski, P. New J Chem 2010, 34, 888–893.
[4] Gupta, A. K.; Acharya, J.; Dubey, D. K.; Kaushik, M. P. J Fluorine Chem 2008, 129, 226.
[5] Gupta, A. K.; Acharya, J.; Pardasani, D.; Dubey, D. K. Tetrahedron Lett 2008, 49, 2232.
[6] Misiura, K.; Szmanowicz, D.; Kusnierczyk, H. Bioorg Med Chem 2001, 9, 1525.
[7] Chworors, A.; Wozniak, L. A. Tetrahedron Lett 1999, 40, 9337.

[8] Bollmark, M.; Zain, R.; Stawinski, J. Tetrahedron Lett 1996, 37, 3537.
[9] Bollmark, M.; Stawinski, J. Chem Commun 1997, 991.
[10] van der Heden van Noort, G. J.; Verhagen, C. P.; van der Horst, M. G.; Overkleeft, H. S.; van der Marel, G. A.; Filippov, D. V. Org Lett 2008, 10, 4461–4464.
[11] Gupta, H. K.; Pardasani, D.; Mazumder, A.; Purohit, A. K.; Dubey, D. K. Tetrahedron Lett 2009, 50, 2697.
[12] Kimura, T.; Murai, T. Chem Lett 2004, 33, 878–879.
[13] Kimura, T.; Murai, T. J Org Chem 2005, 70, 952–959.
[14] Kimura, T.; Murai, T.; Mizuhata, N. Heteroatom Chem 2005, 16, 185–191.
[15] Kimura, T.; Murai, T.; Miwa, A.; Kurachi, D.; Yoshikawa, H.; Kato, S. J Org Chem 2005, 70, 5611–5617.
[16] Kimura, T.; Murai, T. Chem Commun 2005, 4077–4078.
[17] Kimura, T.; Murai, T. Tetrahedron Asymmetry 2005, 16, 3703–3710.
[18] Murai, T.; Matsuoka, D.; Morishita, K. J Am Chem Soc 2006, 128, 4584–4585.
[19] Murai, T.; Inaji, S.; Morishita, K.; Shibahara, F.; Tokunaga, M.; Obora, Y.; Tsuji, Y. Chem Lett 2006, 35, 1424–1425.
[20] Murai, T.; Monzaki, M.; Shibahara, F. Chem Lett 2007, 36, 852–853.
[21] Murai. T. Phosphorus Sulfur Silicon Relat Elem 2008, 183, 889–896.
[22] Murai, T.; Inaji, S.; Takenaka, T. Heteroatom Chem 2009, 20, 255–261.
[23] Murai, T.; Takenaka, T.; Inaji, S.; Tonomura, Y. Chem Lett 2008, 37, 1198–1199.
[24] Jones, S.; Selitsianos, D.; Thompson, K. J.; Toms, S. M. J Org Chem 2003, 68, 5211.
[25] Tanaka, T.; Uchida, S.; Hirose, Y.; Furusawa, A.; Maezaki, N. Tetrahedron 2002, 58, 3493.
[26] Kanyi, C. W.; Doetschman, D. C.; Yang, S. -W.; Schulte, J. T. Microporous Mesoporous Mater 2009, 119, 23–29.
[27] Dabkowski, W.; Tworowska, I. J Chem Soc, Perkin Trans 1 2001, 2462–2469.
[28] Egron, D.; Arzumanov, A. A.; Dyatkina, N. B.; Aubertin, A. -M.; Imbach, J. -L.; Gosselin, G.; Krayevsky, A.; Perigaud, C. Bioorg Chem 2001, 29, 333–344.
[29] Aleksandrova, L. A.; Andronova, V. L.; Karpenko, I. L.; Skoblov Yu, S.; Adani, A.; Galegov, G. A. Russ J Bioorg Chem 2002, 28, 412–418.
[30] Wang, G.; Sakthivel, K.; Rajappan, V.; Bruice, T. W.; Tucker, K.; Fagan, P.; Brooks, J. L.; Hurd, T.; Leeds, J. M.; Cook, P. D. Nucleosides, Nucleotides Nucleic Acids 2004, 23, 317–337.
[31] Guranowski, A.; Wojdyla, A. M.; Pietrowska-Borek, M.; Bieganowski, P.; Khurs, E. N.; Cliff, M. J.; Blackburn, G. M.; Blaziak, D.; Stec, W. J. FEBS Lett 2008, 582, 3152–3158.
[32] Murai, T.; Tanaka, N.; Higashijima, S.; Miura, H. Chem Lett 2009, 38, 668.
[33] Ishihara, K. Tetrahedron 2009, 65, 1085.