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Tetrahedron
Tetrahedron 62 (2006) 1309–1317

Efficient esterification of carboxylic acids and phosphonic acids with trialkyl orthoacetate in ionic liquid

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Received 8 September 2005; accepted 30 September 2005

Abstract—An operationally simple, inexpensive, efficient, and environmentally friendly esterification of various carboxylic acids, phosphonic acids, and phosphinic acids with triethyl orthoacetate or trimethyl orthoacetate under neutral conditions in a typical room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, was successfully carried out to provide the corresponding ethyl esters or methyl esters in high yields.

1. Introduction

Esterification of carboxylic acids is one of the most important functional group conversions in organic synthesis. Therefore, since the Fischer ester synthesis,[1] a number of useful esterification methods catalyzed by Brønsted acids, Lewis acids, ion exchange regins, zeolite, etc. have been reported.[2] Today, environmentally friendly organic synthesis has become much more important and popular, aiming toward green chemistry. Especially, room temperature ionic liquids attract great interest as environmentally friendly reaction media and reaction promotion media for organic synthesis.[3] Thus, these solvents possesses interesting and useful advantages such as negligible vapor pressure, nonflammability, high thermal stability at a wide range of temperature, and easy reusability. These solvents have been successfully used in Friedel-Crafts reaction,[4] hydrogenation,[5] Diels–Alder reactions,[6] Heck, Suzuki, Sonogashira, and olefin metathesis reactions,[7] Michael addition,[8] oxidation,[9] condensation such as Knoevenagel reaction, Fischer esterification, Robinson annulation and related reactions,[10] formation of imines,[11] 1,2-rearrangement,[12] esterification of carboxylic acids and carboxylates,[13] nucleophilic substitution such as the Williamson ether synthesis,[14] etc. Phosphonate esters are also prepared via direct esterification of phosphonic acids with alcohols in the presence of condensing reagents, or the reaction of phosphonochlorides with alcohols, generally.[15]

Here, as a part of our study on environmentally friendly organic synthesis with ionic liquid,[16] we would like to report an operationally simple, inexpensive, efficient, and environmentally friendly esterification of carboxylic acids, phosphonic acids, and phosphinic acids with triethyl orthoacetate or trimethyl orthoacetate under neutral conditions in ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4), 1-butyl-3-methylimidazolium chloride ([bmim]Cl).

2. Results and discussion

2.1. Esterification of carboxylic acids

It is well known that generally triethyl orthoformate and triethyl orthoacetate can be used for the conversion of carbonyl groups to their acetals and ketals.[17] Additionally, triethyl orthoacetate can be used for the esterification of sulfonic acids[18] and carboxylic acids.[18b] However, generally, esterification of carboxylic acids with triethyl orthoacetate requires high temperature, long reaction time, and excess amount of triethyl orthoacetate. For example, 1-naphthoic acid was converted to the desired ethyl ester in 89% yield with triethyl orthoacetate (3.0 equiv) under refluxing conditions in toluene for 24 h. In our present study, when a mixture of 1-naphthoic acid with triethyl orthoacetate (2.0 equiv) in [bmim]PF_6 (2 mL) was heated at 80 °C for 100 min without any additive, the desired ethyl ester was smoothly obtained in 98% yield (entry 1, Table 1). However, this reaction gave rise to low yields under the same conditions in toluene, DMF, DMSO, and even in

Keywords: Esterification; Carboxylic acid; Phosphonic acid; Phosphinic acid; 1-Butyl-3-methylimidazolium hexafluorophosphate; Triethyl orthoacetate; Trimethyl orthoacetate.
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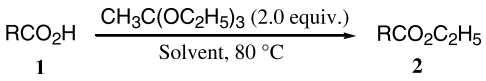
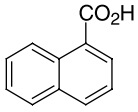
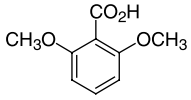
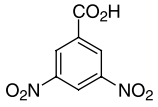
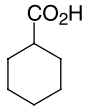
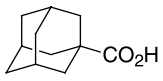
doi:10.1016/j.tet.2005.09.147

Table 1. Solvent effects in ethylation of carboxylic acids with triethyl orthoacetate

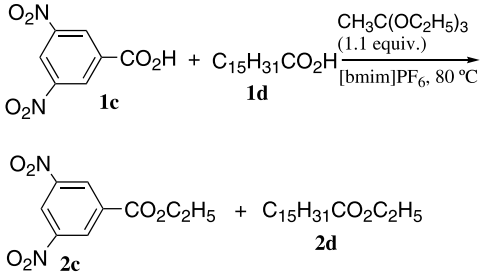


Entry	Carboxylic acid	Time	Yields (%)				
			[bmim]PF_6	Toluene	Neat	DMF	DMSO
1		100 min	98	39	66	23	19 (**2a**)
2		2.5 h	94	19	5	15	23 (**2b**)
3		0.5 h	97	90	98	88	62 (**2c**)
4	$CH_3(CH_2)_{14}CO_2H$	3.5 h[a]	95	66	70	30	28 (**2d**)
5		5 h[a]	94	79	73	39	47 (**2e**)
6		5 h[a]	91	42	22	21	18 (**2f**)

[a] Reaction temperature was 100 °C.

solvent-free conditions. Several examples of esterification with aromatic and aliphatic carboxylic acids by use of our protocol are shown in Table 1, and the formation of the corresponding ethyl esters was much accelerated except for more acidic carboxylic acid such as 3,5-dinitrobenzoic acid (entry 3).[19] Thus, the present system is highly effective, especially for less acidic carboxylic acids. Instead of [bmim]PF_6, other ionic liquids such as [bmim]BF_4, [bmim]Cl were also used as a solvent; however, [bmim]PF_6 showed the most effective reactivity as shown in Table 2 (entries 4–6). Based on these results, other various carboxylic acids were treated with triethyl orthoacetate in [bmim]PF_6, to provide the corresponding ethyl esters in quite good yields as shown in Table 3.

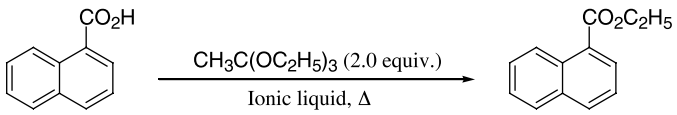
Another interesting advantage of this esterification is the use for sterically hindered carboxylic acids such as 2,4,6-triisopropylbenzoic acid (entry 5), and for amino acid (entry 10) without any racemization as shown in Table 3. Here, ethyl 2,4,6-triisopropylbenzoate cannot be obtained by typical esterification processes such as the Fischer method, DCC method, etc. Moreover, when competitive esterification reaction of 3,5-dinitrobenzoic and palmitic acids was carried out, the corresponding ethyl 3,5-dinitrobenzoate together with recovered palmitic acid was selectively obtained as shown in Eq. 1.



(1)

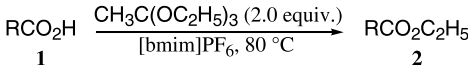
	1c	1d	2c	2d
%	0	79	97	11

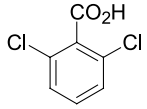
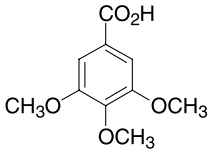
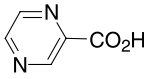
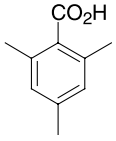
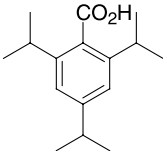
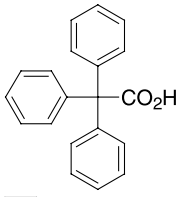
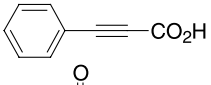
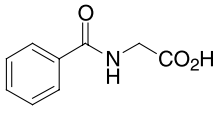
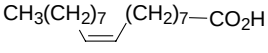
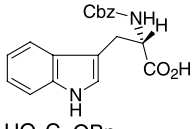
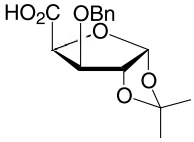
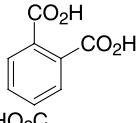
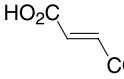
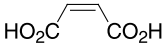
Table 2. Ethylation of 1-naphthoic acid with triethyl orthoacetate in ionic liquids



Entry	Ionic liquid	Time	Temperature (°C)	Yield (%)
1	[bmim]PF_6	24 h	rt	11
2	[bmim]PF_6	15.5 h	40	46
3	[bmim]PF_6	100 min	50	42
4	[bmim]PF_6	100 min	80	98
5	[bmim]BF_4	100 min	80	16
6	[bmim]C1	100 min	80	10

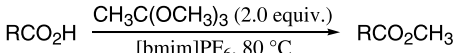
Table 3. Ethylation of various carboxylic acids in [bmim]PF_6

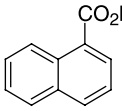
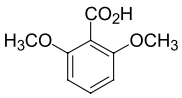
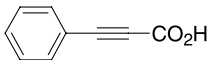


Entry	Carboxylic acid	Time (h)	Yield (%)
1		2	94 (**2g**)
2		4.5	98 (**2h**)
3		3	93 (**2i**)
4		1.5	96 (**2j**)
5		3	97 (**2k**)
6		3	96 (**2l**)
7		0.5	99 (**2m**)
8		3	96 (**2n**)
9		4	90 (**2o**)
10		12	96 (**2p**)[a]
11		2	92 (**2q**)
12		2[b]	99 (**2r**)
13		2.5[b,c]	90 (**2s**)
14		7[b,c]	75 (**2t**)

[a] Optically pure (Dicel Chiralcel OD-H; eluent: hexane/^{i}PrOH=4:1).
[b] TEOA used was 3.0 equiv and yield was for diester.
[c] Reaction temperature was 100 °C.

Table 4. Methylation of carboxylic acids in [bmim]PF_6

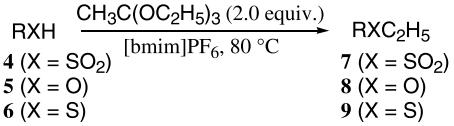


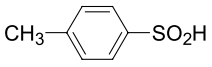
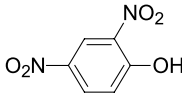
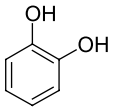
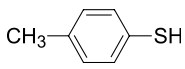
Entry	Carboxylic acids	Time (h)	Yield (%)
1		1.5	96 (**3a**)
2		2	96 (**3b**)
3	$CH_3(CH_2)_{14}CO_2H$	3.5[a]	91 (**3d**)
4		0.5	97 (**3m**)

[a] Reaction temperature was 100 °C.

Trimethyl orthoacetate can be also used for the same esterification reaction of carboxylic acids under the same conditions to form the corresponding methyl esters in high yields as shown in Table 4. Treatment of other protic compounds such as sulfinic acid (**4**), phenols (**5**), and thiol (**6**) with triethyl orthoacetate under the same conditions provided the corresponding ethyl sulfinate (**7**), ethyl ether (**8**), and ethyl thioether (**9**), respectively, in good yields as shown in Table 5. Catechol provided orthoester, not diethyl or monoethyl ether (entry 4).[20]

Table 5. Ethylation of protic compounds in [bmim]PF_6



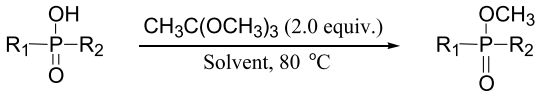
Entry	RXH	Time (h)	Yield (%)
1		0.5	87[a] (**7**)
2		3	88 (**8a**)
3		2	73[b] (**8b**)
4		4	80 (**9**)

[a] Ethyl *p*-touenesulfinate was obtained.
[b] 2-Ethoxy-2-methyl-1,3-benzodioxole was obtained.

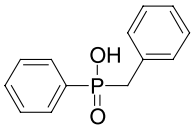
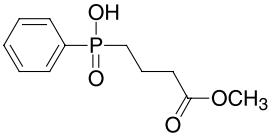
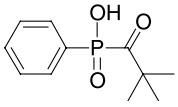
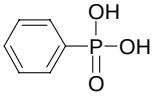
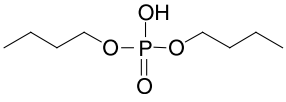
2.2. Esterification of phosphonic acids and phosphinic acids

To date, conversion of phosphonic acids to the corresponding dimethyl phosphonates with trimethyl orthoformate is known;[21] however, it requires high reaction temperature and long reaction time (110 °C, 9 h). In our present study, when a mixture of benzylphenylphosphinic acid (**10A**) with trimethyl orthoacetate (2.0 equiv) in [bmim]PF_6

Table 6. Solvent effect in the methylation of phosphonic and phosphinic acids with trimethyl orthoacetate

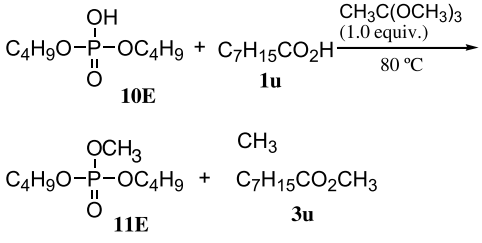


10 **11**

Entry	Phospinic acid	Time (h)	Yields (%)				
			[bmim]PF_6	Toluene	Neat	DMF	DMSO
1		2.5	98	32	70	91	16 (**11A**)
2		1	92	92	93	81	10 (**11B**)
3		1.5	79	71	89	78	40 (**11C**)
4		2[a]	95	78	95	85	13 (**11D**)
5		1	98	70	97	70	29 (**11E**)

[a] This reaction was carried out with 3.5 equiv of TMOA.

(2 mL) was heated at 80 °C for 2.5 h without any additive, the desired methyl ester was smoothly obtained in 98% yield (entry 1, Table 6). Though DMF and solvent-free conditions provided the corresponding methyl ester in good yields, toluene and DMSO showed poor reactivity. Moreover, when phosphinic acids (**10B**), (**10C**), phosphonic acid (**10D**) and dibutyl phosphoric acid (**10E**) were treated with trimethyl orthoacetate, the results indicate that [bmim]PF_6 is the best solvent as shown in Table 6.



(2)

	h / %	**10E**	**1u**	**11E**	**3u**
[bmim]PF_6	1.0	0	93	93	7
Toluene	2.5	23	78	76	21
Solvent free	1.0	61	57	39	35

When triethyl orthoacetate was used instead of trimethyl orthoacetate, ethyl esters were obtained in good yields. However, trimethyl orthoformate showed rather poor reactivity. Unlike [bmim]PF_6, other ionic liquids such as [bmim]BF_4, [bmim]Cl showed poor reactivity again as shown in Table 7. When competitive esterification reaction of dibutylphosphoric acid and octanoic acid was carried out, the selective methylation of phosphoric acid, that is, dibutyl methyl phosphate (93%) and octanoic acid (93%), was observed among [bmim]PF_6, toluene, and solvent-free conditions as shown in Eq. 2.

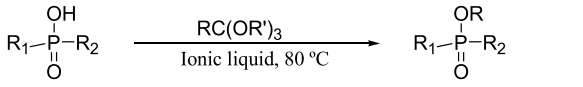
2.3. Recyclic use of 1-butyl-3-methyl imidazolium hexafluorophosphate

Here, room temperature ionic liquid [bmim]PF_6 can be recycled and reused without any loss of chemical yield of esters. Thus, treatment of 1-naphthoic acid (**1a**) and benzylphenylphosphinic acid (**10A**) with triethyl orthoacetate and trimethyl orthoacetate, respectively, in [bmim]PF_6 provided the corresponding ethyl carboxylate and methyl phosphinate in high yields till the fourth regeneration of [bmim]PF_6 as shown in Table 8. After fourth regeneration, [bmim]PF_6 in the esterification of 1-naphthoic acid was almost quantitatively recovered, however, [bmim]PF_6 in the esterification of benzylphenylphosphinic acid was recovered in ~30%. This reason comes from that complete extraction of benzylphenylphosphinate ester with ether from [bmim]PF_6 requires 25 times and therefore [bmim]PF_6 is partly extracted with ether.

3. Conclusion

Thus, an operationally simple, inexpensive, efficient, and environmentally friendly esterification of various carboxylic acids, phosphonic acids, and phosphinic acids with triethyl orthoacetate or trimethyl orthoacetate under

Table 7. Methylation and ethylation of phenylphosphonic acid and benzylphenylphosphonic acid with trialkyl orthoesters in ionic liquids



10

11 (R = CH_3)
12 (R = C_2H_5)

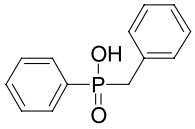
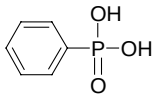
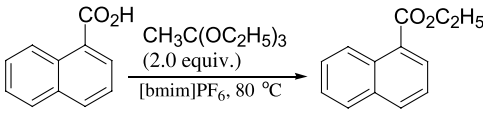
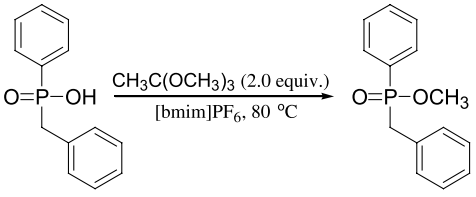
Entry	Substrates	$RC(OR')_{3\ (equiv)}$	Ionic liquid	Time (h)	Yield (%)
1		$CH_3C(OCH_3)_3$ (2.0)	$[bmim]PF_6$	2.5	98 (**11A**)
2		$HC(OCH_3)_3$ (2.0)	$[bmim]PF_6$	2.5	2 (**11A**)
3		$CH_3C(OC_2H_5)_3$ (2.0)	$[bmim]PF_6$	2.5	90 (**12A**)
4		$CH_3C(OCH_3)_3$ (2.0)	$[bmim]BF_4$	2.5	25 (**11A**)
5		$CH_3C(OCH_3)_3$ (2.0)	[bmim]C1	2.5	35 (**11A**)
6		$CH_3C(OCH_3)_3$ (3.5)	$[bmim]PF_6$	2	95 (**11D**)
7		$HC(OCH_3)_3$ (3.5)	$[bmim]PF_6$	2	51 (**11D**)
8		$CH_3C(OC_2H_5)_3$ (3.5)	$[bmim]PF_6$	2	96 (**12D**)
9		$CH_3C(OCH_3)_3$ (3.5)	$[bmim]BF_4$	2	<1 (**11D**)
10		$CH_3C(OCH_3)_3$ (3.5)	[bmim]C1	2	<1 (**11D**)

Table 8. Recycle use of $[bmim]PF_6$



1a **2a**

Regeneration	Time (min)	Yield (%)
0	100	98
1	100	95
2	100	92
3	100	97
4	100	94



10A **11A**

Regeneration	Time (h)	Yield (%)
0	2.5	98
1	2.5	95
2	2.5	94
3	2.5	99
4	2.5	99

neutral conditions in a typical room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, $[bmim]PF_6$, was successfully carried out to provide the corresponding ethyl esters or methyl esters in high yields. The present reactions can be used for esterification of various kinds of carboxylic acids, phosphonic acids, and phosphinic acids even for sterically hindered ones, and $[bmim]PF_6$, can be recycled.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were obtained with JEOL-JNM-LA-400, JEOL-JNM-LA-400s, JEOL-JNM-LA-500, spectrometers. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) in δ units. Mass spectra were recorded on JEOL-HX-110 and JEOL-JMS ATII15 spectrometers. Melting points were determined on Yamato melting points apparatus Model MP-21. Silica Gel 60 (Kanto Kagaku Co.) was used for column chromatography and Wakogel B-5F was used for preparative TLC. Analytical high-performance liquid chromatography (HPLC) was done using a chiral column (4.6 mm×25 cm, Chiralcel OD-H). Optical rotation were measured on a polarimeter.

4.2. Typical procedure for ethylation of carboxylic acid with triethyl orthoacetate in ionic liquid and reuse of ionic liquid

A flask containing 1-butyl-3-methylimidazolium hexafluorophosphate ($[bmim]PF_6$, 2.0 mL) as a solvent was dried under reduced pressure with a vacuum pump for 2 h at 80 °C. Then, 1-naphthoic acid (1.0 mmol) and triethyl orthoacetate (2.0 mmol) were added to the ionic liquid and the obtained mixture was heated at 80 °C under an argon atmosphere. The reaction was monitored by TLC until the starting 1-naphthoic acid disappeared. After 100 min, the mixture was extracted with ether (5×5 mL). The combined ether extract was purified by column chromatography on silica gel (eluent: hexane/EtOAc=9:1) to give pure ethyl 1-naphthoate in 98% yield (bp 120 °C/1 mmHg, lit.[20] 100 °C/0.45 mmHg). After the reaction, ionic liquid was washed with distilled water (5 mL) once and then dried under reduced pressure with a vacuum pump for 2 h at 80 °C, and the ionic liquid was repeatedly used for the same reaction.

4.3. Typical procedure for methylation of carboxylic acid with trimethyl orthoacetate in ionic liquid

A flask containing 1-butyl-3-methylimidazolium hexafluorophosphate ($[bmim]PF_6$, 2.0 mL) as a solvent was dried under reduced pressure with a vacuum pump for 2 h at 80 °C. Then, 1-naphthoic acid (1.0 mmol) and trimethyl orthoacetate (2.0 mmol) were added to the ionic liquid and the obtained mixture was heated at 80 °C under an argon atmosphere. The reaction was monitored by TLC until

the starting 1-naphthoic acid disappeared. After 100 min, the mixture was extracted with ether (5×5 mL). The combined ether extract was purified by column chromatography on silica gel (eluent: hexane/EtOAc=9:1) to give pure methyl 1-naphthoate in 96% yield.

4.4. Competitive reaction of carboxylic acids with triethyl orthoacetate in ionic liquid

A flask containing 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6, 2.0 mL) as a solvent was dried under reduced pressure with a vacuum pump for 2 h at 80 °C. Then, 3,5-dinitrobenzoic acid (1.0 mmol), palmitic acid (1.0 mmol), and triethyl orthoacetate (1.1 mmol) were added to the ionic liquid and the obtained mixture was heated at 80 °C under an argon atmosphere. After 30 min, the mixture was extracted with ether (10×5 mL). The combined ether extract was purified by column chromatography on silica gel (eluent: hexane/EtOAc=5:1) to give ethyl 3,5-dinitrobenzoate (97% yield) and ethyl palmitate (11% yield), together with palmitic acid (79% yield).

Compounds **2a**–**2o**, **2r**–**2t**, **3a**–**3d**, **8a**, **8b**, and **9** were identified with commercially available authentic compounds.

4.4.1. Ethyl 1-naphthoate (2a). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=1.47 (3H, t, J=7.2 Hz), 4.48 (2H, q, J=7.2 Hz), 7.52 (2H, m), 7.62 (1H, t, J=7.2 Hz), 7.88 (1H, d, J=8.2 Hz), 8.02 (1H, d, J=8.2 Hz), 8.18 (1H, dd, J=7.2, 1.5 Hz), 8.91 (1H, d, J=8.2 Hz); IR (neat) 2980, 1710, 1510, 1280, 1240, 1200, 1140, 780 cm^{-1}.

4.4.2. Ethyl 2,6-dimethoxybenzoate (2b). Colorless solid; mp 69–70 °C; ^{1}H NMR ($CDCl_3$) δ=1.37 (3H, t, J=7.2 Hz), 3.82 (6H, s), 4.39 (2H, q, J=7.2 Hz), 6.56 (2H, d, J=8.4 Hz), 7.28 (1H, t, J=8.4 Hz); IR (KBr) 2990, 1730, 1590, 1480, 1430, 1290, 1250, 1110, 1075, 780 cm^{-1}.

4.4.3. Ethyl 3,5-dinitrobenzoate (2c). Yellow solid; mp 92–93 °C; ^{1}H NMR ($CDCl_3$) δ=1.48 (3H, t, J=7.2 Hz), 4.53 (2H, q, J=7.2 Hz), 9.18 (2H, d, J=2.1 Hz), 9.23 (1H, t, J=2.1 Hz); IR (KBr) 3000, 1730, 1540, 1350, 1280, 740 cm^{-1}.

4.4.4. Ethyl palmitate (2d). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.9 Hz), 1.23–1.34 (27H, m), 1.62 (2H, quin, J=7.5 Hz), 2.29 (2H, t, J=7.5 Hz), 4.12 (2H, q, J=7.2 Hz); IR (neat) 2930, 2850, 1740, 1470, 1180 cm^{-1}.

4.4.5. Ethyl cyclohexanecarboxylate (2e). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=1.17–1.34 (3H, m), 1.25 (3H, t, J=7.2 Hz), 1.43 (2H, qd, J=12.3, 2.7 Hz), 1.64 (1H, m), 1.76 (2H, m), 1.90 (2H, dd, J=12.3, 2.7 Hz), 2.28 (1H, tt, J=11.4, 3.6 Hz), 4.11 (2H, q, J=7.2 Hz); IR (neat) 2930, 2850, 1730, 1450, 1380, 1310, 1250, 1170, 1040 cm^{-1}.

4.4.6. Ethyl 1-adamantanecarboxylate (2f). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=1.24 (3H, t, J=7.2 Hz), 1.71 (6H, t, J=14.5 Hz), 1.88 (6H, d, J=2.9 Hz), 2.01 (3H, s), 4.10 (2H, q, J=7.2 Hz); IR (neat) 2910, 1730, 1450, 1320, 1230, 1180, 1080, 1030, 740 cm^{-1}.

4.4.7. Ethyl 2,6-dichlorobenzoate (2g). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=1.42 (3H, t, J=7.2 Hz), 4.47 (2H, q, J=7.2 Hz), 7.25–7.34 (3H, m); IR (neat) 2980, 1740, 1560, 1440, 1270, 1140, 1060, 800, 780 cm^{-1}.

4.4.8. Ethyl 3,4,5-trimethoxybenzoate (2h). Colorless solid; mp 52 °C; ^{1}H NMR ($CDCl_3$) δ=1.40 (3H, t, J=7.2 Hz), 3.91 (3H, s), 3.92 (6H, s), 4.38 (2H, q, J=7.2 Hz), 7.3 (2H, s); IR (KBr) 2960, 1710, 1590, 1410, 1330, 1230, 1110, 990, 760 cm^{-1}.

4.4.9. Ethyl pyrazinecarboxylate (2i). Colorless solid; mp 48–49 °C; ^{1}H NMR ($CDCl_3$) δ=1.47 (3H, t, J=7.2 Hz), 4.53 (2H, q, J=7.2 Hz), 8.74 (1H, dd, J=2.4, 1.6 Hz), 8.77 (1H, d, J=2.4 Hz), 9.33 (1H, d, J=1.6 Hz); IR (KBr) 2980, 1740, 1370, 1310, 1280, 1160, 1120, 1020, 860, 780 cm^{-1}.

4.4.10. Ethyl 2,4,6-trimethylbenzoate (2j). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=1.38 (3H, t, J=7.2 Hz), 2.28 (3H, s), 2.29 (6H, s), 4.38 (2H, q, J=7.2 Hz), 6.85 (2H, d, J=0.5 Hz); IR (neat) 2980, 1730, 1610, 1270, 1080 cm^{-1}.

4.4.11. Ethyl 2,4,6-triisopropylbenzoate (2k). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=1.24 (18H, m), 1.35 (3H, t, J=7.2 Hz), 2.87 (3H, m), 4.36 (2H, q, J=7.2 Hz), 7.01 (2H, s); IR (neat) 2960, 1730, 1460, 1250, 1080 cm^{-1}.

4.4.12. Ethyl triphenylacetate (2l). Colorless solid; mp 117–118 °C; ^{1}H NMR ($CDCl_3$) δ=1.20 (3H, t, J=7.2 Hz), 4.28 (2H, q, J=7.2 Hz), 7.18 (6H, m), 7.27 (9H, m); IR (KBr) 2980, 1740, 1370, 1310, 1280, 1160, 1120, 1020, 860, 780 cm^{-1}.

4.4.13. Ethyl phenylpropiolate (2m). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=1.36 (3H, t, J=7.2 Hz), 4.31 (2H, q, J=7.2 Hz), 7.38 (2H, t, J=7.4 Hz), 7.45 (1H, tt, J=7.4, 1.7 Hz), 7.59 (2H, d, J=7.4 Hz); IR (neat) 2980, 2210, 1710, 1490, 1370, 1280, 1190, 1020, 760 cm^{-1}.

4.4.14. Ethyl hippurate (2n). Colorless solid; mp 61–62 °C; ^{1}H NMR ($CDCl_3$) δ=1.32 (3H, t, J=7.2 Hz), 4.27 (4H, m), 6.68 (1H, s), 7.45 (2H, t, J=7.4 Hz), 7.53 (1H, t, J=7.4 Hz), 7.82 (2H, d, J=7.4 Hz); IR (KBr) 3340, 1760, 1640, 1530, 1200 cm^{-1}.

4.4.15. Ethyl oleate (2o). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz), 1.23–1.37 (23H, m), 1.62 (2H, quin, J=7.3 Hz), 2.01 (4H, m), 2.29 (2H, t, J=7.6 Hz), 4.12 (2H, q, J=7.1 Hz), 5.35 (2H, m); IR (neat) 2930, 2850, 1740, 1460, 1180 cm^{-1}.

4.4.16. *N*-Benzyloxycarbonyl-L-tryptophan ethyl ester (2p). Colorless solid; mp 85–86 °C (lit.[22] mp 85–87 °C); ^{1}H NMR ($CDCl_3$) δ=1.19 (3H, t, J=7.2 Hz), 3.31 (2H, d, J=5.4 Hz), 4.12 (2H, m), 4.70 (1H, m), 5.10 (2H, m), 5.32 (1H, d, J=8.0 Hz), 6.94 (1H, d, J=2.0 Hz), 7.08 (1H, t, J=8.0 Hz), 7.18 (1H, t, J=8.0 Hz), 7.33 (6H, m), 7.53 (1H, d, J=8.0 Hz), 8.09 (1H, s, broad); $[\alpha]_D^{21}$ +37.9 (c 1.0, $CHCl_3$); IR (KBr) 3360, 1740, 1710, 1530, 1220 cm^{-1}.

4.4.17. α-D-Xylofuranuronic acid, 1,2-*O*-(1-methylethylidene)-3-*O*-(phenylmethyl)-, ethyl ester (2q). Colorless oil; ^{1}H NMR ($CDCl_3$) δ=1.23 (3H, t, J=7.2 Hz), 1.32

(3H, s), 1.48 (3H, s), 4.14–4.31 (3H, m), 4.53 (2H, d, $J=12.1$ Hz), 4.64 (2H, m), 4.81 (1H, d, $J=3.7$ Hz), 6.09 (1H, d, $J=3.7$ Hz), 7.31 (5H, m); ^{13}C NMR ($CDCl_3$) $\delta=14.01$ (s), 26.19 (s), 26.79 (s), 61.11 (d), 72.08 (d), 79.42 (t), 81.56 (t), 82.65 (t), 105.55 (t), 112.17 (q), 127.50 (t), 127.81 (t), 128.25 (t), 136.81 (q), 167.61 (q); IR (neat) 2990, 2940, 1770, 1730, 1380, 1210, 1120, 1080, 1030 cm^{-1}; HRMS (FAB): Obsd M+H=323.1469, Calcd for $C_{17}H_{23}O_6$ M+H=323.1495.

4.4.18. Diethyl phthalate (2r). Colorless oil; ^{1}H NMR ($CDCl_3$) $\delta=1.37$ (3H, t, $J=7.3$ Hz), 4.37 (2H, q, $J=7.3$ Hz), 7.53 (2H, m), 7.73 (2H, m); IR (neat) 2980, 1730, 1280, 1120, 1070, 750 cm^{-1}.

4.4.19. Diethyl maleate (2s). Colorless oil; ^{1}H NMR ($CDCl_3$) $\delta=1.31$ (6H, t, $J=7.2$ Hz), 4.26 (4H, q, $J=7.2$ Hz), 6.24 (2H, s); IR (neat) 2980, 1730, 1210, 1180, 1030 cm^{-1}.

4.4.20. Diethyl fumarate (2t). Colorless oil; ^{1}H NMR ($CDCl_3$) $\delta=1.32$ (6H, t, $J=7.2$ Hz), 4.26 (4H, q, $J=7.2$ Hz), 6.85 (2H, s); IR (neat) 2980, 1720, 1300, 1260, 1150, 1040 cm^{-1}.

4.4.21. Methyl 1-naphthoate (3a). Colorless oil; ^{1}H NMR ($CDCl_3$) $\delta=4.01$ (3H, s), 7.52 (2H, m), 7.62 (1H, t, $J=8.2$ Hz), 7.89 (1H, d, $J=8.2$ Hz), 8.03 (1H, d, $J=8.2$ Hz), 8.19 (1H, dd, $J=7.2$, 1.5 Hz), 8.91 (1H, d, $J=8.2$ Hz); IR (neat) 2950, 1720, 1510, 1280, 1250, 1200, 1140, 780 cm^{-1}.

4.4.22. Methyl 2,6-dimethoxybenzoate (3b). Colorless solid; mp 88–89 °C; ^{1}H NMR ($CDCl_3$) $\delta=3.82$ (6H, s), 3.91 (3H, s), 6.56 (2H, d, $J=8.3$ Hz), 7.28 (1H, t, $J=8.3$ Hz); IR (KBr) 3000, 1730, 1590, 1480, 1290, 1250, 1110, 1075, 790 cm^{-1}.

4.4.23. Methyl palmitate (3c). Colorless oil; ^{1}H NMR ($CDCl_3$) $\delta=0.88$ (3H, t, $J=6.9$ Hz), 1.23–1.33 (24H, m), 1.62 (2H, quin, $J=7.4$ Hz), 2.30 (2H, t, $J=7.4$ Hz), 3.67 (3H, s); IR (neat) 2920, 2850, 1740, 1460, 1180 cm^{-1}.

4.4.24. Methyl phenylpropiolate (3d). Colorless oil; ^{1}H NMR ($CDCl_3$) $\delta=3.85$ (3H, s), 7.38 (2H, t, $J=7.4$ Hz), 7.45 (1H, tt, $J=7.4$, 1.9 Hz), 7.59 (2H, d, $J=7.4$ Hz); IR (neat) 2220, 1710, 1490, 1430, 1290, 1200, 1170, 760 cm^{-1}.

4.4.25. Ethyl *p*-toluenesulfinate (7). Colorless oil; bp 107 °C/1 mmHg (lit.[23] 75–76 °C/0.1 mmHg); ^{1}H NMR ($CDCl_3$) $\delta=1.28$ (3H, t, $J=7.0$ Hz), 2.43 (3H, s), 3.72 (1H, m), 4.10 (1H, m), 7.34 (2H, d, $J=8.0$ Hz), 7.60 (1H, dt, $J=8.0$, 1.7 Hz); IR (neat) 2980, 1130, 1010, 880, 820, 710 cm^{-1}.

4.4.26. 1-Ethoxy-2,4-dinitrobenzene (8a). Colorless solid; mp 83–84 °C; ^{1}H NMR ($CDCl_3$) $\delta=1.55$ (3H, t, $J=7.0$ Hz), 4.33 (2H, q, $J=7.0$ Hz), 7.19 (1H, d, $J=9.3$ Hz), 8.42 (1H, dd, $J=9.3$, 2.7 Hz), 8.73 (1H, d, $J=2.7$ Hz); IR (KBr) 3120, 1610, 1530, 1350, 1290, 1160, 1020, 740 cm^{-1}.

4.4.27. 2-Ethoxy-2-methyl-1,3-benzodioxole (8b). Colorless oil; ^{1}H NMR ($CDCl_3$) $\delta=1.20$ (3H, t, $J=7.1$ Hz), 1.81 (3H, s), 3.59 (2H, q, $J=7.1$ Hz), 6.82 (4H, m); IR (neat) 2980, 1490, 1260, 1180, 1050, 980, 880, 740 cm^{-1}.

4.4.28. Ethyl *p*-tolyl sulfide (9). Colorless oil; ^{1}H NMR ($CDCl_3$) $\delta=1.28$ (3H, t, $J=7.3$ Hz), 2.32 (3H, s), 2.90 (2H, d, $J=7.3$ Hz), 7.10 (2H, d, $J=8.0$ Hz), 7.25 (2H, d, $J=8.0$ Hz); IR (neat) 2980, 2940, 1490, 1450, 1260, 1090, 810 cm^{-1}.

4.5. Typical procedure for ethylation of phosphonic acid with triethyl orthoacetate in ionic liquid and reuse of ionic liquid

A flask containing 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6, 2.0 mL) as a solvent was dried under reduced pressure with a vacuum pump for 2 h at 80 °C. Then, benzylphenylphosphinic acid (1.0 mmol) and trimethyl orthoacetate (2.0 mmol) were added to the ionic liquid and the obtained mixture was heated at 80 °C under an argon atmosphere. The reaction was monitored by TLC until the starting benzylphenylphosphinic acid desappeared. After 2.5 h, the mixture was extracted with Et_2O (25×5 mL). The combined Et_2O extract was purified by column chromatography on silica gel (eluent: hexane/EtOAc, 1:1) to give pure methyl benzylphenylphosphinate in 98% yield.

Compounds **12A**, **11D**, and **12D** were identified with commercially available authentic compounds.

4.5.1. Methyl benzylphenylphosphinate (11A). Colorless solid; mp 80–82 °C (lit.[24] mp 87–93 °C); ^{1}H NMR ($CDCl_3$) $\delta=3.30$ (2H, d, $J=18$ Hz), 3.64 (3H, d, $J=11$ Hz), 7.09 (2H, m), 7.20 (3H, m), 7.41 (2H, m), 7.52 (1H, m), 7.58 (2H, m); ^{31}P NMR ($CDCl_3$, H_3PO_4) $\delta=41.28$ (s); IR (neat) 1439, 1215, 1026, 750, 695 cm^{-1}.

4.5.2. Ethyl benzylphenylphosphinate (12A). Colorless solid; mp 54–55 °C; ^{1}H NMR ($CDCl_3$) $\delta=1.28$ (3H, t, $J=18.1$ Hz), 3.29 (2H, d, $J=11$ Hz), 3.88 (1H, m), 4.07 (1H, m), 7.09 (2H, m), 7.20 (3H, m), 7.40 (2H, m), 7.51 (1H, m), 7.60 (2H, m); ^{31}P NMR ($CDCl_3$, H_3PO_4) $\delta=39.52$ (s); IR (neat) 1438, 1213, 1031, 749, 693 cm^{-1}.

4.5.3. Methyl (2-carbomethoxyethyl)phenylphosphinate (11B). Colorless oil; bp 150 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) $\delta=2.25$ (2H, m), 2.58 (2H, m), 3.64 (3H, d, $J=11$ Hz), 3.63 (3H, s), 7.52 (2H, m), 7.58 (1H, m), 7.79 (2H, m); ^{13}C NMR ($CDCl_3$) $\delta=24.52$ (d), 26.33 (d), 51.11 (s), 51.79 (s), 128.64 (t), 129.10 (q), 131.56 (t), 132.50 (t), 172.35 (q); ^{31}P NMR ($CDCl_3$, H_3PO_4) $\delta=44.12$ (s); IR (neat) 1735, 1439, 1214, 1026, 740, 697 cm^{-1}; HRMS (FAB): Obsd M+H=243.0790, Calcd for $C_{11}H_{16}O_4P$ M+H=243.0786.

4.5.4. Methyl (2,2-dimethyl-1-oxopropyl)phenylphosphinate (11C). Colorless oil; bp 120 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) $\delta=1.29$ (9H, s), 3.77 (3H, d, $J=11$ Hz), 7.46–7.63 (3H, m), 7.84 (2H, m); ^{13}C NMR ($CDCl_3$) $\delta=25.06$ (s), 47.31 (q), 51.11 (s), 51.99 (s), 127.79 (q), 128.61 (t), 132.54 (t), 133.10 (t), 217.29 (q); ^{31}P NMR ($CDCl_3$, H_3PO_4)

δ=20.26 (s); IR (neat) 1716, 1680, 1440, 1230, 1024, 724, 694 cm^{-1}; HRMS (FAB): Obsd M+H=241.0992, Calcd for $C_{12}H_{18}O_3P$ M+H=240.0915.

4.5.5. Dimethyl phenylphosphonate (11D). Colorless oil; ^1H NMR ($CDCl_3$) δ=3.77 (6H, d, J=11 Hz), 7.48 (2H, m), 7.58 (1H, m), 7.81 (2H, m); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ=21.10 (s); IR (neat) 1440, 1249, 1018, 750, 696 cm^{-1}.

4.5.6. Diethyl phenylphosphonate (12D). Colorless oil; ^1H NMR ($CDCl_3$) δ=1.33 (6H, d, J=7.0 Hz), 4.03–4.21 (4H, m), 7.47 (2H, m), 7.56 (1H, m), 7.82 (2H, m); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ=39.52 (s); IR (neat) 1440, 1247, 1017, 748, 696 cm^{-1}.

4.5.7. Dibutyl methyl phosphate (11E). Colorless oil; bp 80 °C/1 mmHg (lit.[25] bp 85–87 °C/2 mmHg); ^1H NMR ($CDCl_3$) δ=0.94 (6H, t, J=7.5 Hz), 1.42 (4H, m), 1.67 (4H, m), 3.76 (3H, d, J=11 Hz), 4.05 (4H, m); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ=−0.22 (s); IR (neat) 1265, 1022 cm^{-1}.

Acknowledgements

Financial support from a Grant-in-Aid for Scientific Research (No. 13554028) from the Ministry of Education, Science, Sports and Culture of Japan is gratefully acknowledged.

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