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PII: S0040-4020(20)30228-3

DOI: https://doi.org/10.1016/j.tet.2020.131107

Reference: TET 131107

To appear in: *Tetrahedron*

Received Date: 23 December 2019

Revised Date: 15 February 2020

Accepted Date: 6 March 2020

Please cite this article as: Xu C, Li T, Jiang P, Zhang Y-j, Practical synthesis of phosphonium salts with orthoformates and their application as flame retardants in polycarbonate, *Tetrahedron* (2020), doi: https://doi.org/10.1016/j.tet.2020.131107.

Graphical Abstract

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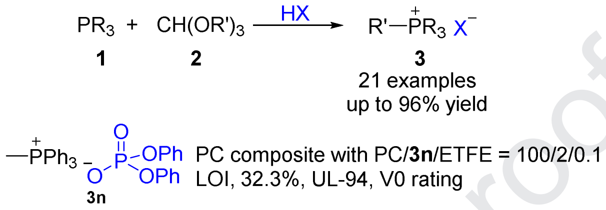

21 examples
up to 96% yield

PC composite with PC/**3n**/ETFE = 100/2/0.1
LOI, 32.3%, UL-94, V0 rating

Tetrahedron
journal homepage: www.elsevier.com

Practical synthesis of phosphonium salts with orthoformates and their application as flame retardants in polycarbonate

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Synthetic method
Phosphonium salts
Salification
Flame retardants
Polycarbonate

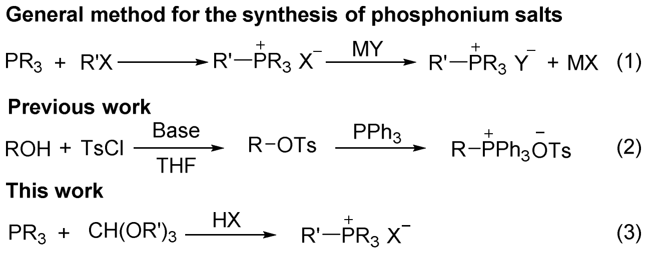
ABSTRACT

An efficient and practical approach to phosphonium salts has been developed. By the reaction of phosphines and different acid sources with orthoformates in one-step operation, the process allowed rapid access to phosphonium salts with diverse counterions in high yield after the purification by recrystallization. The flame retardant performance in PC has also been examined by blending several phosphonium salts to PC respectively. Phosphonium phosphates showed excellent flame retardancy in PC with only 2 phr blending.

1. Introduction

Phosphonium salts are important precursors for the Wittig olefination,[1] and they are also useful phase-transfer catalysts[2] for catalytic organic transformations. Phosphonium salts have also been widely used in supercapacitors,[3] dye-sensitised solar cells,[4] corrosion inhibitors,[5] lubricants,[6] and organic transformations as green media.[7] It is well known that polymeric materials containing phosphonium salts have been extensively applied to a variety of antimicrobial-relevant areas.[8] In this context, the development of efficient methods for the synthesis of phosphonium salts is an important objective in organic synthesis. The most common approach to phosphonium salts includes reaction of phosphines with alkyl halides to form phosphonium halide salts followed by anion exchange with metal salts and removal of metal halides (Scheme **1**, eq. **1**).[9] In most application area for the phosphonium salts, the weakly coordination anions, such as BF_4^-, PF_6^-, SbF_6^- and $(CF_3SO_2)_2N^-$, are needed,[10] and the remaining metal halides are known to deteriorate their properties for use.[11] Although this common synthetic method is efficient for making phosphonium salts, the separation of inorganic metal halides in the anion exchange step remains challenging. Therefore, the development of practical and direct approaches to phosphonium salts, that avoid the use of halides, are highly appealing.

Flame retardant performance has become an important index for the application of polymeric materials.[12] Blending modification of polymeric materials with flame retardants (FRs) is a general approach to give the fire-resistance property for polymers. Halogen-based FRs are the most widely used organic FRs in the world due to their low price, good stability, low addition amount and good compatibility with synthetic resin materials.[13] However, large amount of smoke is released during the fire and the released hydrogen halide is easy to cause secondary disasters.[14] FRs based on organic phosphorus compounds are known to be one of the most promising candidates that can replace the halogen-based FRs. To date, great numbers of phosphorus-containing FRs have been developed due to their good ability in flame retardancy and environmental friendliness.[12a,15] Most recently, our group have developed several organic phosphonium salts as FRs,[16] which showed excellent flame retardant performance while they were applied to polycarbonate (PC) and poly(ethylene-co-vinyl acetate) (EVA). The phosphonium salts were synthesized by sulfonate formation from alcohols with p-toluenesufonic chloride in the presence of base followed by salification with triphenylphosphine (Scheme **1**, eq. **2**). However, the method needs two steps operation and their anion part are restricted by the sulfonate species.



Scheme 1. Synthesis of phosphonium salts

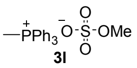
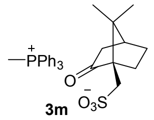
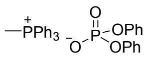
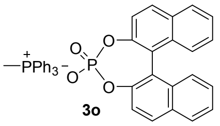
Mcnulty and Das reported the reaction of methyl orthoformate with phosphonium HBr salts to generate methylphosphonium bromide.[17] However, the method just limited in the formation of bromide salts. Most recently, Park and coworkers reported the reaction of imidazoles and acids with orthoformates to afford imidazolium salts with diverse counterions.[18] Herein we present an efficient and practical method via the reaction of phosphines and acids with orthoformates in one step operation, which allows rapid access phosphonium salts with diverse counterions in high yields. In addition, the flame retardant performance in PC has also been examined by blending several phosphonium salts to PC respectively.

2. Results and Discussion

Initially, we conducted the reaction of triphenylphosphine (**1a**) and methyl orthoformate (**2a**) with various acid sources (ASs) at 110 °C (Table 1). Firstly, we tried the reaction with halogen anions, such as ammonium chloride, ammonium bromide and ammonium iodide, and found that the reactivity highly depends on the anion source. Thus, the reaction with ammonium chloride gave corresponding phosphonium chloride **3a** in 51% yield in 12 h, whereas phosphonium bromide **3b** and iodide **3c** were obtained in high yields in shorter reaction time. Non-coordination anion BF_4^- and PF_6^- could also be introduced when the reaction of **1a** and **2a** with HBF_4 and HPF_6 or their ammonium salts to give corresponding phosphonium salts **3d** and **3e** in acceptably high isolated yields. The reaction of **1a** and **2a** with $HN(SO_2CF_3)_2$ in 2 h gave phosphonium salt **3f** in 95% yield. Various sulfonate anions could be introduced under the reaction conditions to give **3g**-**3m** in high yields. Notably, the reaction of **1a** and **2a** with sulfuric acid or ammonium sulfate to give phosphonium methyl sulfate **3l** in high yield. In addition, chiral sulfonate **3m** could also be obtained in moderate yield. The reaction conditions also tolerated to prepare phosphonium phosphate, thus phosphonium diphenyl phosphate **3n** and phosphonium binaphthyl phosphate **3o** could be obtained in high yields.

Table 1. The reaction of triphenylphosphine (**1a**) and methyl orthoformate (**2a**) with different acid sources[a]

$$\underset{\textbf{1a}}{PPh_3} + \underset{\textbf{2a}}{CH(OMe)_3} \xrightarrow[110\ ^{o}C]{\text{acid source (AS)}} \underset{\textbf{3}}{—\overset{+}{P}Ph_3\ \overset{-}{X}}$$

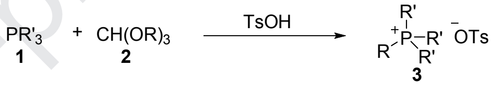
$—\overset{+}{P}Ph_3\overset{-}{Cl}$ **3a** AS: NH_4Cl, RT: 12 h, 51% yield	$—\overset{+}{P}Ph_3\overset{-}{Br}$ **3b** AS: NH_4Br, RT: 4 h, 96% yield	$—\overset{+}{P}Ph_3\ \overset{-}{I}$ **3c** AS: NH_4I, RT: 1 h, 92% yield	$—\overset{+}{P}Ph_3\overset{-}{BF_4}$ **3d** AS: HBF_4, RT: 1 h, 79% yield AS: NH_4BF_4, RT: 4 h, 81% yield
$—\overset{+}{P}Ph_3\overset{-}{PF_6}$ **3e** AS: HPF_6, RT: 1 h, 78% yield AS: NH_4PF_6, RT: 6 h, 79% yield	$—\overset{+}{P}Ph_3\overset{-}{N}(SO_2CF_3)_2$ **3f** AS: $HN(SO_2CF_3)_2$, RT: 2 h, 95% yield	$—\overset{+}{P}Ph_3\overset{-}{OTf}$ **3g** AS: TfOH, RT: 10 h, 82% yield	$—\overset{+}{P}Ph_3\overset{-}{OMs}$ **3h** AS: MsOH, RT: 12 h,94% yield
$—\overset{+}{P}Ph_3\overset{-}{OTs}$ **3i** AS: TsOH, RT: 12 h, 91% yield Large scale,[b] RT: 24 h, 89% (79.8 g)	$—\overset{+}{P}Ph_3PhS\overset{-}{O_3}$ **3j** AS: $PhSO_3H$, RT: 8 h, 89% yield	$—\overset{+}{P}Ph_3EtS\overset{-}{O_3}$ **3k** AS: $EtSO_3H$, RT: 12 h, 95% yield	 $—\overset{+}{P}Ph_3\ \overset{-}{O}-S(=O)_2-OMe$ **3l** AS: H_2SO_4, RT: 2 h, 84% yield AS: $(NH_4)_2SO_4$, RT: 36 h, 92% yield
 **3m** AS: L-camphorsulfonic acid, RT: 48 h, 66% yield	 **3n** AS: diphenyl phosphate, RT: 24 h, 94% yield Large scale,[b] RT: 48h, 69% (72.7 g)	 **3o** AS: binaphthyl phosphate, RT: 30 h, 81% yield	

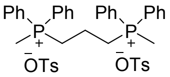
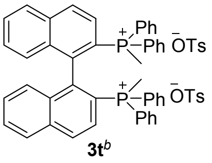
[a] General reaction conditions: **1a** (1 mmol), **2a** (5 mmol), AS (1 mmol), at 110 °C (sealed). The yields are of isolated materials after recrystallization. [b] Large scale reactions were carried out as **1a** (0.2 mol), **2a** (1 mol), AS (0.2 mmol), at 110 °C.

In order to demonstrate the synthetic utility of the present process, the large-scale transformations were tested. Significantly, the reactions of **1a** and **2a** with 4-toluenesulfonic acid and diphenyl hydrogen phosphate in 0.2 mol scale afforded **3i** in 89% (79.8 g) yield and **3n** in 69% (72.7g) yield respectively after the purification by recrystallization.

After successfully realization of the synthesis of methyl triphenylphosphonium salts with various counterions, we subsequently turned our attention to examining the reaction scope with different orthoformates and phosphines using TsOH as an acid source. As shown in Table **2**, ethyl, n-propyl and i-propyl group could be introduced to afford corresponding phosphonium salts **3p**-**3r** in high yields, even though higher reaction temperature and longer reaction time were needed. The reaction of bisphosphines, DPPP and BINAP, also proceeded smoothly to give bisphosphonium salts **3s** and **3t** in moderate yields. Tributyl methylphosphonium tosylate **3u** could also be obtained in 76% yield under the reaction conditions.

Table 2. The reaction of phosphines **1** and orthoformates **2** with 4-toluenesulfonic acid[a]


$$\underset{\textbf{1}}{PR'_3} + \underset{\textbf{2}}{CH(OR)_3} \xrightarrow{\text{TsOH}} \underset{\textbf{3}}{R-\overset{+}{P}R'_3\ \overset{-}{OTs}}$$

$Et—\overset{+}{P}Ph_3\overset{-}{OTs}$ **3p** RT: 24 h, 120 °C, 91% yield	$^{n}Pr—\overset{+}{P}Ph_3\overset{-}{OTs}$ **3q** RT: 68 h, 130 °C, 77% yield	$^{i}Pr—\overset{+}{P}Ph_3\overset{-}{OTs}$ **3r** RT: 90 h, 130 °C, 82% yield
 **3s**[b] RT: 12 h, 110 °C, 78% yield	 **3t**[b] RT: 12 h, 110 °C, 51% yield	$—\overset{+}{P}(^{n}Bu)_3\overset{-}{OTs}$ **3u** RT: 6 h, 110 °C, 76% yield

[a] General reaction conditions: **1** (1 mmol), **2** (5 mmol), TsOH (1 mmol). [b] The reactions carried out with **1** (1 mmol), **2** (10 mmol), TsOH (2 mmol). The yields are of isolated materials after recrystallization.

With synthesized phosphonium salts in hand, we next chose several phosphonium salts to examine their flame retardant performance in PC. The samples were prepared by blending of PC, each phosphonium salt **3** and anti-dripping agent, ethylene tetrafluoroethylene (ETFE) with a weight ratio of 100:2:0.1 in a Haake Rheocord 90 internal mixer at 210 °C for 10 min. The obtained mixtures were subsequently pressed into sheets of 3 mm which could be easily processed into desired sample shape.

Firstly, in order to investigate the thermal stability of the flame-retardant PC/phosphonium salt composites, thermogravimetric analysis (TGA) was carried out under N_2 atmosphere (Fig.**1**). As shown in Figure **1** and Table **3**, $T_{5\%}$ of PC composites were decreased in comparing with that of virgin PC, which means the processed PC decomposed earlier comparing to virgin PC. The result of T_{max} indicated that max decomposing temperature of the PC composites also came earlier. The PC composites with phosphonium phosphates **3n** and **3o**, and phosphonium tosylates **3m**, **3r**, **3s**, and **3t** showed relatively high $T_{5\%}$ and T_{max}, which slightly decreased than virgin PC. The residual at 800 °C of PC/phosphonium composites have no big change than that of virgin PC. These results indicated that although the addition of phosphonium salts to PC lead to earlier thermal degradation of the PC composites, there have no obvious deterioration of thermal stability after blending phosphonium salts to PC.

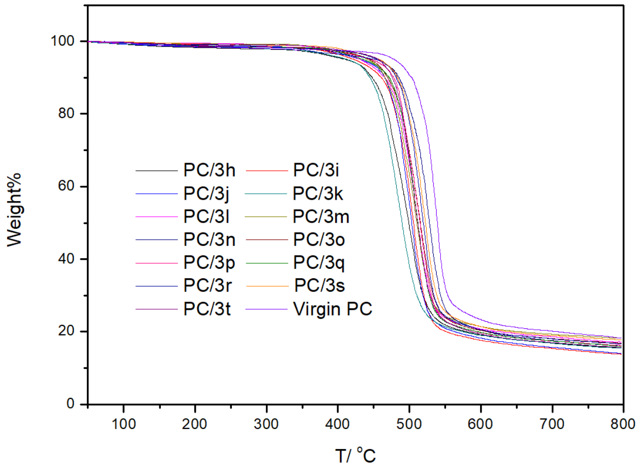


Figure 1. Thermogram of PC/phosphonium salts composites.

Table 3. TGA data of PC/phosphonium salts composites

Sample	$T_{5\%}{}^{a}$/□	$T_{max}{}^{b}$/□	Residual at 800□/wt%
Virgin PC	468.9	537.6	18.3
PC/**3h**	411.3	500.4	15.6
PC/**3i**	422.9	505.0	13.8
PC/**3j**	432.1	502.8	14.1
PC/**3k**	413.4	483.5	15.4
PC/**3l**	431.8	509.6	17.2
PC/**3m**	442.3	510.7	18.2
PC/**3n**	456.6	522.1	16.0
PC/**3o**	444.9	514.9	16.8
PC/**3p**	447.3	515.9	16.2
PC/**3q**	436.3	509.9	16.1
PC/**3r**	453.4	519.5	16.7
PC/**3s**	458.4	521.7	17.8
PC/**3t**	457.1	509.6	15.7

[a] $T_{5\%}$ indicated the temperature when the tested sample lose 5% of its mass. [b] T_{max} indicated the temperature when the speed of mass-loss reached its maximum.

In order to investigate the flame retardancy of the phosphonium salts, the limiting oxygen index (LOI) values and vertical burning rating (UL-94) for the PC/phosphonium salts were examined. As illustrated in Table **4**, virgin PC is a kind of flammable polymer with no rating in UL-94 and low LOI value (25.6%). The LOI value got greatly improved when only 2 phr (parts of per hundreds of rubber or resin) of the phosphonium salts were added into the PC blends. Especially when phosphonium phosphate **3n** and **3o** were added, the LOI value increased to 32.3% and 31.7% respectively, and they both reached the V-0 rating. Other phosphonium salts all showed positive effect towards flame retardancy, but failed to reach V-1 rating in UL-94. In view of only 2 phr loading of phosphonium salts in the blend, they worked quite well during burning process.

Table 4. LOI and UL-94 results of PC/ phosphonium salts composites

Sample	UL-94 rating	LOI(%)	ΔLOI（%）
Virgin	NR	25.6	-
PC/**3h**	V2	30.3	4.7
PC/**3i**	V2	27.7	2.1
PC/**3j**	V2	27.7	2.1
PC/**3k**	V2	28.9	3.3
PC/**3l**	V2	29.6	4.0
PC/**3m**	V2	30.7	5.1
PC/**3n**	V0	32.3	6.7
PC/**3o**	V0	31.7	6.1
PC/**3p**	V2	26.9	1.3
PC/**3q**	V2	29.6	4.0
PC/**3r**	V2	26.0	0.4
PC/**3s**	V2	28.2	2.6
PC/**3t**	V2	27.0	1.4

3. Conclusion

In conclusion, we have developed an efficient and practical method for the synthesis of phosphonium salts via the one-step reaction of phosphines and excessed orthoformates with equivalent of acid salts without additional solvents. The process allowed rapid access to phosphonium salts with diverse counterions in high yield. The synthetic utility was demonstrated by the large-scale transformations. In addition, several phosphonium salts have been applied as flame retardants for PC. The all tested PC/**3** composites with only 2 phr loading of phosphonium salts showed good thermal stability and flame retardancy. Especially, the PC composites with phosphonium phosphates **3n** and **3o** showed excellent flame retardant properties, which reach to V-0 rating. Further studies on expending this phosphonium salts formation process to other salts formation and the application of phosphonium salts as flame retardants to other polymers are currently underway, and will be reported in due course.

4. Experimental

4.1. Materials

Polycarbonate (PC) was purchased from LG Chem., with a density of 1.20 g/cm^3 and a melt index of 22 g/10 min. Ethylene tetrafluoro-ethylene (ETFE) was supplied by Dongyue Group Ltd. All of the chemicals were bought and used directly without further purification.

4.2. General procedure for the synthesis of phosphonium salts 3

As shown in the table **1** and **2**, phosphine, acid and orthoformate in a mol ratio of 1:1:5 were added to the reaction tube. The reaction mixture was stirred at 110 °C. After the completion of the reaction, the reaction mixture was cooled to room temperature, and the excessed orthoformate was evaporated under reduced pressure. The obtained residue was recrystallized with dichloromethane and ethyl acetate, and washed with ethyl acetate and petroleum ether. The product was dried in a vacuum oven at 60 °C overnight to obtain desired pure phosphonium salts.

*4.3. Methyltriphenylphosphonium chloride (**3a**)*

Yield: 51%; light brown solid; 145-147 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.69 (m, 15H), 3.27 (d, *J* = 13.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.08, 135.06, 133.16, 133.08, 130.42, 130.32, 119.41, 118.71, 10.42, 9.97; ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.82; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1143.

*4.4. Methyltriphenylphosphonium bromide (**3b**)*

Yield: 96%; white solid; 149-151 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.83–7.69 (m, 15H), 3.27 (d, J = 13.3 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.08, 135.06, 133.27, 133.18, 130.44, 130.34, 119.41, 118.70, 11.06, 10.61; ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.82; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1144. Calcd. for Br$^-$:78.9189, Found: 78.9175.

*4.5. Methyltriphenylphosphonium iodide (**3c**)*

Yield: 92%; light yellow solid; 144-147 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.85–7.77 (m, 3H), 7.76 – 7.70 (m, 12H), 3.17 (d, J = 13.2 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.12, 135.10, 133.15, 133.06, 130.43, 130.33, 118.98, 118.27, 11.60, 11.14; ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.82; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1143. Calcd. for I$^-$: 126.9050, Found: 126.9044.

*4.6. Methyltriphenylphosphonium fluoroborate (**3d**)*

Yield: 79% (AS: HBF_4), 81% (AS: NH_4BF_4); light yellow solid; 148-150 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81–7.71 (m, 3H), 7.70–7.62 (m, 12H), 2.88 (dd, J = 13.4, 4.2 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.18, 135.15, 133.08, 133.00, 130.51, 130.41, 119.36, 119.34, 118.66, 118.64, 9.26, 8.79; ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.50, 21.43; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1141. Calcd. for BF_4^-: 87.0035, Found: 87.0027.

*4.7. Methyltriphenylphosphonium hexafluorophosphate (**3e**)*

Yield: 78% (AS: HPF_6), 79% (AS: NH_4PF_6); white solid; 178-180 ^{o}C; ^{1}H NMR (500 MHz, DMSO) δ 7.91–7.87 (m, 3H), 7.78–7.73 (m, 12H), 3.14 (d, J = 14.7 Hz, 3H); ^{13}C NMR (125 MHz, DMSO) δ 134.85, 134.83, 133.28, 133.20, 130.17, 130.07, 120.27, 119.57, 7.47, 7.03; ^{31}P NMR (202 MHz, DMSO) δ 22.66, -133.66, -137.17, -140.68, -144.20, -147.71, -151.22, -154.74; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1145. Calcd. for PF_6^-: 144.9647, Found: 144.9644.

*4.8. Methyltriphenylphosphonium bis((trifluoromethyl)sulfonyl)amide (**3f**)*

Yield: 95%; white solid; 115-117 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.85–7.81 (m, 3H), 7.72–7.71 (m, 6H), 7.70–7.59 (m, 6H), 2.82 (d, J = 13.2 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.38, 135.36, 132.97, 132.89, 130.61, 130.51, 121.10, 119.03, 118.32, 9.72, 9.25; ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.22; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1145. Calcd. for $N(SO_2CF_3)_2^-$: 279.9178, Found: 279.9178.

*4.9. Methyltriphenylphosphonium trifluoromethanesulfonate (**3g**)*

Yield: 82%; white solid; 130-132 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81–7.77 (m, 3H), 7.70–7.61 (m, 12H), 2.85 (d, J = 13.2 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.21, 135.18, 133.06, 132.98, 130.51, 130.41, 122.02, 119.25, 118.54, 9.63, 9.17; ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.44; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1142. Calcd. for $CF_3O_3S^-$: 148.9526, Found: 148.9519.

*4.10. Methyltriphenylphosphonium methanesulfonate (**3h**)*

Yield: 94%; white solid; 45-47 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.83–7.79 (m, 3H), 7.75–7.68 (m, 12H), 3.11 (d, J = 13.3 Hz, 3H), 2.64 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 134.94, 134.91, 133.06, 132.97, 130.33, 130.22, 119.40, 118.69, 39.25, 9.64, 9.18; ^{31}P NMR (162 MHz, CDCl$_3$) δ 22.82; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1145. Calcd. for $CH_3O_3S^-$: 94.9808, Found: 94.9756.

*4.11. Methyltriphenylphosphonium 4-methylbenzenesulfonate (**3i**)*

Yield: 91%; white solid; 57-59 ^{o}C; Large scale: The reaction was carried out with 0.2 mol of triphenylphosphine, 1 mol of trimethyl orthoformate and 0.2 mol of p-toluenesulfonic acid at 110 ^{o}C for 24 h. The reaction mixture was cooled to room temperature, and the excessed orthoformate was evaporated under reduced pressure. The obtained residue was recrystallized with dichloromethane and ethyl acetate, and washed with ethyl acetate and petroleum ether. The product was dried in a vacuum oven at 60 °C overnight to obtain **3i** in 89% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75–7.62 (m, 17H), 7.02 (d, J = 7.4 Hz, 2H), 3.04–3.00 (m, 3H), 2.28 (d, J = 4.8 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 144.30, 138.20, 134.82, 134.80, 133.00, 132.91, 130.25, 130.15, 128.05, 125.91, 119.33, 119.31, 118.63, 118.61, 21.10, 9.45, 8.99; ^{31}P NMR (162 MHz, CDCl$_3$) δ 22.69; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1118. Calcd. for $C_7H_7O_3S^-$: 171.0121, Found:171.0095.

*4.12. Methyltriphenylphosphonium benzenesulfonate (**3j**)*

Yield: 89%; White solid; 142-145 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.85–7.63 (m, 17H), 7.27–7.55 (m, 3H), 3.12 (d, J = 13.3 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.06, 134.94, 134.91, 133.16, 133.07, 130.38, 130.27, 128.69, 127.62, 126.08, 119.55, 118.85, 9.71, 9.25; ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.75; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1140. Calcd. for $C_6H_5O_3S^-$:141.0016, Found:141.0019.

*4.13. Methyltriphenylphosphonium ethanesulfonate (**3k**)*

Yield: 95%; White solid; 80-82 ^{o}C; ^{1}H NMR (500 MHz, CDCl3) δ 7.82–7.68 (m, 15H), 3.15 (d, J = 13.3 Hz, 3H), 2.75 (q, J = 7.5 Hz, 2H), 1.26 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 134.92, 134.90, 133.12, 133.04, 130.35, 130.25, 119.52, 118.82 , 45.51, 9.88, 9.75, 9.30; ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.85; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1110. Calcd. for $C_2H_5O_3S^-$: 108.9965, Found: 108.9947.

*4.14. Methyltriphenylphosphonium methyl sulphate (**3l**)*

Yield: 84% (AS: H_2SO_4), 92% (AS: NH_4SO_4); light yellow solid; 150-153 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.82–7.78 (m, 3H), 7.73–7.68 (m, 12H), 3.65 (s, 3H), 3.08 (d, J = 13.3 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.05, 135.02, 133.21, 133.13, 130.46, 130.36, 119.61, 118.90, 54.24, 9.64, 9.18; ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.85; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1124. Calcd. for $CH_3O_4S^-$:110.9758, Found:110.9710.

*4.15. Methyltriphenylphosphonium ((1R,4S)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (**3m**)*

Yield: 66%; light yellow solid; 190-192 ^{o}C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81 – 7.67 (m, 15H), 3.29 (d, J = 14.7 Hz, 1H), 3.16 (d, J = 13.3 Hz, 3H), 2.90 – 2.83 (m, 1H), 2.74 (d, J = 14.7 Hz, 1H), 2.27 (dt, J = 18.0, 4.0 Hz, 1H), 1.98 – 1.91 (m, 2H), 1.80 (d, J = 18.0 Hz, 1H), 1.62 – 1.56 (m, 1H), 1.30 – 1.24 (m, 1H), 1.13 (s, 3H), 0.80 (s, 3H).; ^{13}C NMR (125 MHz, CDCl$_3$) δ 217.15, 134.83, 134.81, 133.12, 133.10, 133.04, 133.01, 130.28, 130.18, 119.58, 118.88, 58.54, 47.54, 46.62, 42.78, 42.76, 42.50, 26.95, 24.30, 20.21, 19.74, 9.68, 9.22; ^{31}P NMR (202 MHz, CDCl$_3$) δ 21.87; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1140, Found: 277.1110. Calcd. for $C_{10}H_{15}O_4S^-$: 231.0697, Found: 231.0674.

*4.16. Methyltriphenylphosphonium diphenyl phosphate (**3n**)*

Yield: 94%; white solid; 125-127 ^{o}C; Large scale: The reaction was carried out with 0.2 mol of triphenylphosphine, 1 mol of trimethyl orthoformate and 0.2 mol of diphenylphosphoric acid at 110 °C for 48 h. The reaction mixture was cooled to room temperature, and the excessed orthoformate was evaporated under reduced pressure. The obtained residue was recrystallized with dichloromethane and ethyl acetate, and washed with ethyl acetate and petroleum ether. The product was dried in a vacuum oven at 60 °C overnight to obtain **3n** in 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.69 (m, 3H), 7.63–7.56 (m, 12H), 7.23 (d, *J* = 8.0 Hz, 4H), 7.10 (t, *J* = 7.7 Hz, 4H), 6.87 (t, *J* = 7.3 Hz, 2H), 2.96 (d, *J* = 13.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.96, 153.90, 134.75, 134.72, 132.93, 132.85, 130.19, 130.08, 128.54, 121.62, 120.17, 120.13, 119.33, 118.63, 9.14, 8.69; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.75, -9.17; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1140, Found: 277.1120. Calcd. for $C_{12}H_{10}O_4P^-$:249.0317, Found:249.0303.

*4.17. Methyltriphenylphosphonium dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-olate 4-oxide (**3o**)*

Yield: 81%; White solid; 143-145 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 1H NMR (500 MHz, Chloroform-d) δ 7.81–7.78 (m, 4H), 7.60–7.56 (m, 3H), 7.47–7.41 (m, 14H), 7.32–7.28 (m, 4H), 7.14–7.11 (m, 2H), 2.67 (d, *J* = 13.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.55, 150.48, 134.88, 134.86, 133.22, 133.13, 133.12, 132.81, 130.92, 130.36, 130.26, 129.81, 128.22, 127.18, 125.59, 124.21, 122.94, 122.92, 122.60, 122.58, 119.74, 119.03, 9.20, 8.75; ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.80, 21.77, 6.34; HRMS (ESI-MS): Calcd. for $C_{19}H_{18}P^+$: 277.1141, Found: 277.1140. Calcd. for $C_{20}H_{12}O_4P^-$:347.0479, Found:347.0476.

*4.18. Ethyltriphenylphosphonium 4-methylbenzenesulfonate (**3p**)*

Yield: 91%; light pink solid; 104-107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.72 (m, 11H), 7.67–7.64 (m, 6H), 7.05 (d, *J* = 7.9 Hz, 2H), 3.58–3.51 (m, 2H), 2.29 (s, 3H), 1.30 (dt, *J* = 20.1, 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.39, 138.25, 134.79, 134.77, 133.39, 133.31, 130.41, 130.34, 130.24, 128.09, 125.98, 118.25, 117.56, 21.13, 16.06, 15.65, 6.53, 6.48; ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.04; HRMS (ESI-MS): Calcd. for $C_{20}H_{20}P^+$: 291.1297, Found: 291.1297. Calcd. for $C_7H_7O_3S^-$:171.0121, Found:171.0132.

*4.19. Triphenyl(propyl)phosphonium 4-methylbenzenesulfonate (**3q**)*

Yield: 77%; light yellow solid; 130-132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.74 (m, 11H), 7.68–7.64 (m, 6H), 7.05 (dd, *J* = 8.1, 2.0 Hz, 2H), 3.54–3.48 (m, 2H), 2.30 (s, 3H), 1.68–1.58 (m, 2H), 1.15 (td, *J* = 7.2, 1.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.12, 138.53, 134.81, 134.79, 133.57, 133.54, 133.49, 133.46, 130.42, 130.39, 130.32, 128.23, 126.15, 126.12, 118.78, 118.09, 23.66, 23.26, 21.25, 16.48, 16.44, 15.20, 15.06; ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.90; HRMS (ESI-MS): Calcd. for $C_{21}H_{22}P^+$:305.1454, Found:305.1454. Calcd. for $C_7H_7O_3S^-$:171.0121, Found:171.0123.

*4.20. Isopropyltriphenylphosphonium 4-methylbenzenesulfonate (**3r**)*

Yield: 82%; white solid; 191-193 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94–7.88 (m, 8H), 7.75–7.64 (m, 9H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.03–4.96 (m, 1H), 2.32 (d, *J* = 3.1 Hz, 3H), 1.31 (dd, *J* = 19.0, 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.44, 138.54, 134.55, 134.53, 133.83, 133.75, 130.40, 130.31, 128.33, 126.17, 118.04, 117.38, 21.26, 20.46, 20.09, 16.21, 16.19; ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.90; HRMS (ESI-MS): Calcd. for $C_{21}H_{22}P^+$: 305.1454, Found: 305.1453. Calcd. for $C_7H_7O_3S^-$: 171.0121, Found: 171.0124.

*4.21. Propane-1,3-diylbis(methyldiphenylphosphonium) 4-methylbenzenesulfonate (**3s**)*

Yield: 78%; white solid; 155-157 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.79 (m, 12H), 7.66–7.54 (m, 12H), 7.12 (d, *J* = 8.2 Hz, 4H), 3.72–3.66 (m, 4H), 2.62 (d, *J* = 13.3 Hz, 6H), 2.33 (s, 6H), 2.06 – 2.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.90, 139.03, 134.38, 132.44, 132.40, 132.36, 130.29, 130.24, 130.19, 130.18, 130.14, 130.09, 128.56, 128.54, 125.87, 125.85, 119.46, 118.77, 22.82, 22.67, 22.38, 22.23, 21.25, 16.30, 6.86, 6.41; ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.45; HRMS (ESI-MS): Calcd. for $C_{29}H_{32}P_2^{2+}$:442.1968, Found: 221.0994. Calcd. for $C_7H_7O_3S^-$: 171.0121, Found: 171.0123.

*4.22. [1,1'-binaphthalene]-2,2'-diylbis (methyldiphenylphosphonium) 4-methylbenzenesulfo-nate (**3t**)*

Yield: 51%; light yellow solid; 138-140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48–8.30 (m, 2H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.80–7.45 (m, 20H), 7.34 (td, *J* = 7.8, 3.6 Hz, 4H), 7.11–6.96 (m, 8H), 6.81 (t, *J* = 7.7 Hz, 2 H), 6.60 (d, *J* = 8.6 Hz, 2H), 2.30 (s, 6H), 2.25 (d, J = 12.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.17, 138.74, 135.31, 135.29, 135.11, 134.78, 133.56, 133.47, 132.56, 132.46, 132.28, 132.20, 130.75, 130.70, 130.64, 130.28, 130.18, 129.11, 129.01, 128.92, 128.47, 128.38, 126.28, 126.05, 119.71, 119.00, 118.83, 118.31, 118.13, 117.63, 21.27, 10.62, 10.18; ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.48; HRMS (ESI-MS): Calcd. for $C_{46}H_{38}P_2^{2+}$: 652.2438, Found: 326.1223. Calcd. for $C_7H_7O_3S^-$: 171.0121, Found: 171.0123.

*4.23. Tributyl(methyl)phosphonium 4-methylbenzenesulfonate (**3u**)*

Yield: 76%; colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 2.33 (s, 3H), 2.25–2.19 (m, 6H), 1.90 (dd, *J* = 13.5, 5.1 Hz, 3H), 1.45–1.41 (m, 12H), 0.91 (t, *J* = 6.8 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.91, 139.44, 139.42, 128.48, 125.94, 125.92, 23.75, 23.63, 23.48, 23.44, 21.19, 19.92, 19.53, 13.35; ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.79; HRMS (ESI-MS): Calcd. for $C_{13}H_{30}P^+$: 217.2080, Found: 217.2079. Calcd. for $C_7H_7O_3S^-$: 171.0121, Found: 171.0107.

4.24. PC/phosphonium salt composites preparation

PC, phosphonium salts and anti-dripping agent (Ethylene tetrafluoro-ethylene ,ETFE) were dried in vacuum heating drying oven before processing. PC, phosphonium salts and ETFE were mixed in a weight ratio of 100:2:0.1 [2 phr (parts of per hundreds of rubber or resin)] in a Haake Rheocord 90 internal mixer (Haake, Bersdorff, Germany) at 210 °C for 10 min. The obtained mixtures were subsequently pressed into sheets of 3 mm which could be easily processed into desired sample shape.

4.25. Thermal behaviour of PC/phosphonium salt composites

The thermogravimetric analysis (TGA) of PC/phosphonium salt composites was performed with a NETZSCH TG 209 thermal analyzer at a heating rate of 20 °C/min and the temperature ranged from 50 °C to 800 °C. TGA was carried out in N_2 atmosphere, and specimen mass for TGA was 5 mg.

4.26. Flame retardancy of PC/ phosphonium salt composites

The limiting oxygen index (LOI) values were tested by using an HC-2 type instrument (Nanjing Jiangning Analytical Instrument Factory, China) on the sheets of 120×6.5×3 mm^3 according to ASTM D2863-77. The vertical burning rating (UL-94) was tested by using a CZF-1 type instrument (Nanjing Analytical Instrument Factory, China) on the sheets of 127×12.7×3 mm^3 according to ANSI/UL-94.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (21574079, 21871179). We thank the Instrumental Analysis Center of Shanghai Jiao Tong University for HRMS analysis.

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An efficient and practical approach to phosphonium salts has been developed. By the reaction of phosphines and different acid sources with orthoformates in one-step operation, the process allowed rapid access to phosphonium salts with diverse counterions in high yield after the purification by recrystallization. Some phosphonium salts have been applied as flame retardant in polycarbonate.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: