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The Reaction of Triphenylphosphonium or Triphenylarsonium Salts with Aldehyde: Effect of the Counteranion on their Reactivity

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Abstract—Some acetonyltriphenylphosphonium, methoxycarbonylmethyltriphenylphosphonium salts and their triphenylarsonium analogues could undergo Wittig reaction with aldehyde in good yields. Their reactivity was counteranion-dependent and was arranged in the following order: p-TsO^-, $Br^- \ll CF_3CO_2^- \ll ClCH_2CO_2^- < PhCO_2^-$, HCO_2^-, $MeCO_2^-$. The proton-coupled ^{13}C NMR splitting patterns of the α-methylene groups provided a valuable information to predict their reactivity with aldehyde. Only those onium salts without C–H coupling could undergo Wittig reaction. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The reaction of aldehyde with triphenylphosphonium ylide is an important method of C–C double bond formation.[1] Interestingly, we found that the mono-substituted ozonides could react with stable triphenylphosphonium ylides (1.3 mol equiv.) to give *trans*-α, β-unsaturated carbonyl compounds in high yields (Fig. 1).[2] The plausible mechanism of this reaction is described as follows. The ozonide ring proton is regioselectively deprotonated by triphenylphosphonium ylide, followed by ring fragmentation to give both aldehyde **A** and triphenylphosphonium formate (**B**).[3] The phosphonium formate **B** is proposed to react with aldehyde to give the desired product (Fig. 1). To the best of our knowledge, there is no precedent literature which has reported the Wittig reaction from triphenylphosphonium salts in the absence of base.[1] The reaction rate of the stable phosphonium ylide with ketone is facilitated by the presence of a catalytic amount of benzoic acid. The role of benzoic acid in the reaction has been postulated to result from the protonation of the carbonyl oxygen, making it more susceptible to be attacked by the ylide.[4] In order to demonstrate the possibility of our proposed mechanism in Fig. 1, it is interesting to prepare compound **B** and investigate its reaction with aldehyde. In this report, we have prepared a variety of triphenylphosphonium and

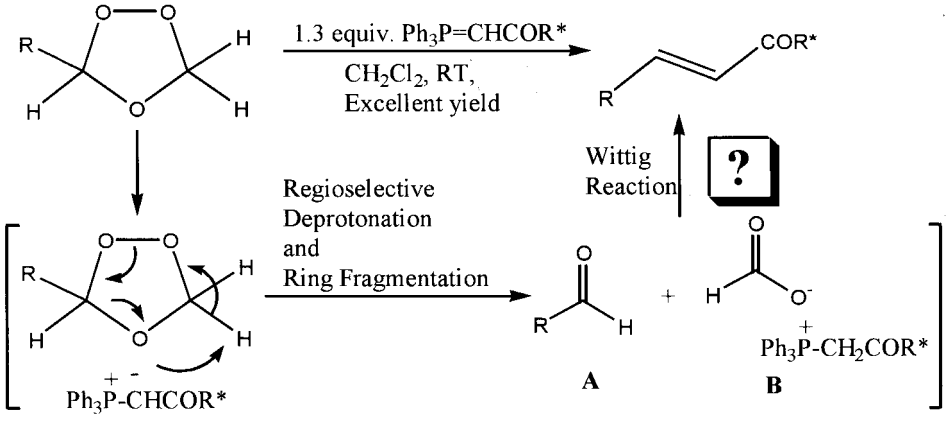

Figure 1. Proposed mechanism for the reaction of ozonide and stable phosphonium ylide.

Keywords: triphenylphosphonium ylide; triphenylarsonium ylide; triphenylphosphonium salts; triphenylarsonium salts; counteranion; Wittig reaction; ozonide.

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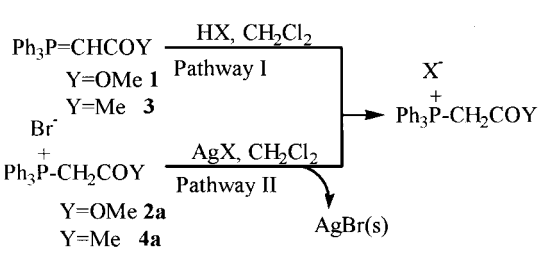
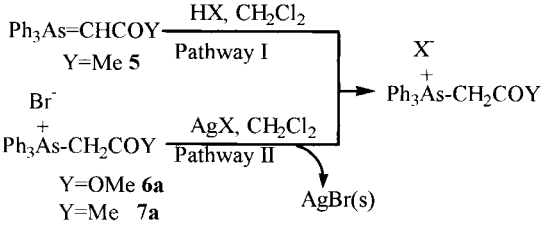


X=	Y = OMe	Y= Me
$MeCO_2$	**2b**	**4b**
$PhCO_2$	**2c**	**4c**
HCO_2	**2d**	**4d**
$ClCH_2CO_2$	**2e**	**4e**
CF_3CO_2	**2f**	-
p-TsO	**2g**	**4g**

Scheme 1.



X=	Y = OMe	Y= Me
$MeCO_2$	**6b**	**7b**
$PhCO_2$	**6c**	**7c**
HCO_2	-	**7d**
CF_3CO_2	**6f**	**7f**

Scheme 2.

triphenylarsonium salts and disclose the fact that the reactivity of these salts with aldehyde is counteranion-dependent.

Results and Discussion

Preparation of triphenylphosphonium and triphenylarsonium salts

The triphenylphosphonium salts with different kinds of counteranions (**2b–2g** and **4b–4g**) were prepared by the following two methods (Scheme 1). One was the addition of protic acid (1 mol equiv.) to the corresponding phosphonium ylides (i.e. **1** and **3**) as shown in Pathway I. The other was the reaction of triphenylphosphonium bromides (**2a** and **4a**) with silver salts via anion exchange in CH_2Cl_2 as shown in Pathway II. The silver bromide precipitate was removed by filtration (Scheme 1). Both methods afforded the corresponding triphenylphosphonium salts in excellent yields. However, we were unable to prepare compound **4f** by either method. Similarly, the triphenylarsonium salts with different kinds of counteranions (**6b–6f** and **7b–7d**) were also prepared by Pathway I and II in excellent yields as shown in Scheme 2. We were unable to prepare acetonyltriphenylarsonium ylide ($Ph_3As{=}CHCO_2Me$) so that arsonium salts **6b–6f** could only be prepared by Pathway II (Scheme 2). All these onium salts were fully characterized by the ^1H and ^{13}C NMR, mass spectroscopy and elemental analysis.

Table 1. The characteristic off-resonance decoupled splitting patterns for the α-carbon of the phosphonium salts and the results of their reactions with aldehyde **8**

Entry	$Ph_3^+PC(\alpha)H_2Y\ X^-$ [a]			^{13}C of α-CH_2 [b]				Reaction with aldehyde **8**		p*K*a of HX
	Y=	X=		δ (ppm)	Splitting pattern	$^1J_{H-C}$ (Hz)	$^1J_{P-C}$ (Hz)	Time (h)	Yield[c] (%)	
1	CO_2Me	Br	**2a**	32.7	td	133.7	57.0	24	6	−9
2	CO_2Me	$MeCO_2$	**2b**	30.4	d	0	105.8	0.5	92	4.75
3	CO_2Me	$PhCO_2$	**2c**	29.9	d	0	124.2	0.5	95	4.20
4	CO_2Me	HCO_2	**2d**	30.1	d	0	110.6	0.5	90	3.75
5	CO_2Me	$ClCH_2CO_2$	**2e**	30.6	d	0	85.1	4	89	2.87
6	CO_2Me	CF_3CO_2	**2f**	31.2	td	134.0	58.0	24	30[d]	0.23
7	CO_2Me	*p*-TsO	**2g**	31.3	td	134.5	58.1	24	0[e]	−7
8	COMe	Br	**4a**	40.6	td	130.0	58.4	24	0[f]	−9
9	COMe	$MeCO_2$	**4b**	56.2	d	0	106.0	4	90	4.75
10	COMe	$PhCO_2$	**4c**	56.5	d	0	105.6	4	90	4.20
11	COMe	HCO_2	**4d**	57.3	d	0	104.2	4	81	3.75
12	COMe	$ClCH_2CO_2$	**4e**	59.7	d	0	99.8	7	85	2.87
13	COMe	*p*-TSO	**4g**	39.0	td	130.8	59.5	24	0[g]	−7

[a] All the phosphonium salts were characterized by ^1H NMR, ^{13}C NMR, IR, mass and elemental analysis.
[b] Cα was a carbon between phosphorus and carbonyl. The ^{13}C NMR (50 MHz) spectra were taken in $CDCl_3$ at rt.
[c] Only *E*-isomer was formed in each case.
[d] 49% of aldehyde was recovered.
[e] 71% of aldehyde was recovered.
[f] 73% of aldehyde was recovered and 6% yield of 2,4,6-tris(2-phenylethyl)-1,3,5-trioxane was isolated.
[g] 73% of aldehyde was recovered.

Table 2. The characteristic off-resonance decoupled splitting patterns for the α-carbon of the arsonium salts and the results of their reactions with aldehyde **8**

Entry	$Ph_3^+AsC(\alpha)H_2Y\ X^-$[a]			^{13}C of α-CH_2[b]			Reaction with aldehyde **8**		p*K*a of HX
	Y=	X=		δ (ppm)	Splitting pattern	$^1J_{H-C}$ (Hz)	Time (h)	Yield[c] (%)	
1	CO_2Me	Br	**6a**	33.8	t	141.1	24	0	−9
2	CO_2Me	$MeCO_2$	**6b**	32.1	s	0	0.5	93	4.75
3	CO_2Me	$PhCO_2$	**6c**	29.7	s	0	0.5	92	4.20
4	CO_2Me	CF_3CO_2	**6f**	32.2	t	141.2	24	16[d]	0.23
5	COMe	Br	**7a**	40.2	t	136.5	24	6	−9
6	COMe	$MeCO_2$	**7b**	57.0	s	0	2	94	4.75
7	COMe	$PhCO_2$	**7c**	55.5	s	0	2	87	4.20
8	COMe	HCO_2	**7d**	56.0	s	0	2.5	83	3.75
9	COMe	CF_3CO_2	**7f**	42.2	t	137.3	24	14[e]	0.23

[a] All the phosphonium salts were characterized by ^1H NMR, ^{13}C NMR, IR, mass and elemental analysis.
[b] Cα was a carbon between arsenic and carbonyl. The ^{13}C NMR (50 MHz) spectra were taken in $CDCl_3$ at rt.
[c] Only *E*-isomer was formed in each case.
[d] 75% of aldehyde was recovered.
[e] 71% of aldehyde was recovered.

Reactivity of the triphenylphosphonium and arsonium salts with aldehyde

The typical procedure to test the reactivity of the triphenylphosphonium salts with aldehyde is described as follows. A mixture of triphenylphosphonium salts (1.1 mol equiv.) and 3-phenylpropanal (**8**) in dichloromethane was stirred at room temperature and the results were shown in Table 1. The triphenylphospnonium bromides (i.e. **2a** and **4a**) or *p*-toluenesulfonates (i.e. **2g** and **4g**) almost did not react with aldehyde at rt for 24 h, as expected (Entries 1, 7, 8 and 13, Table 1). However, when the counteranions were

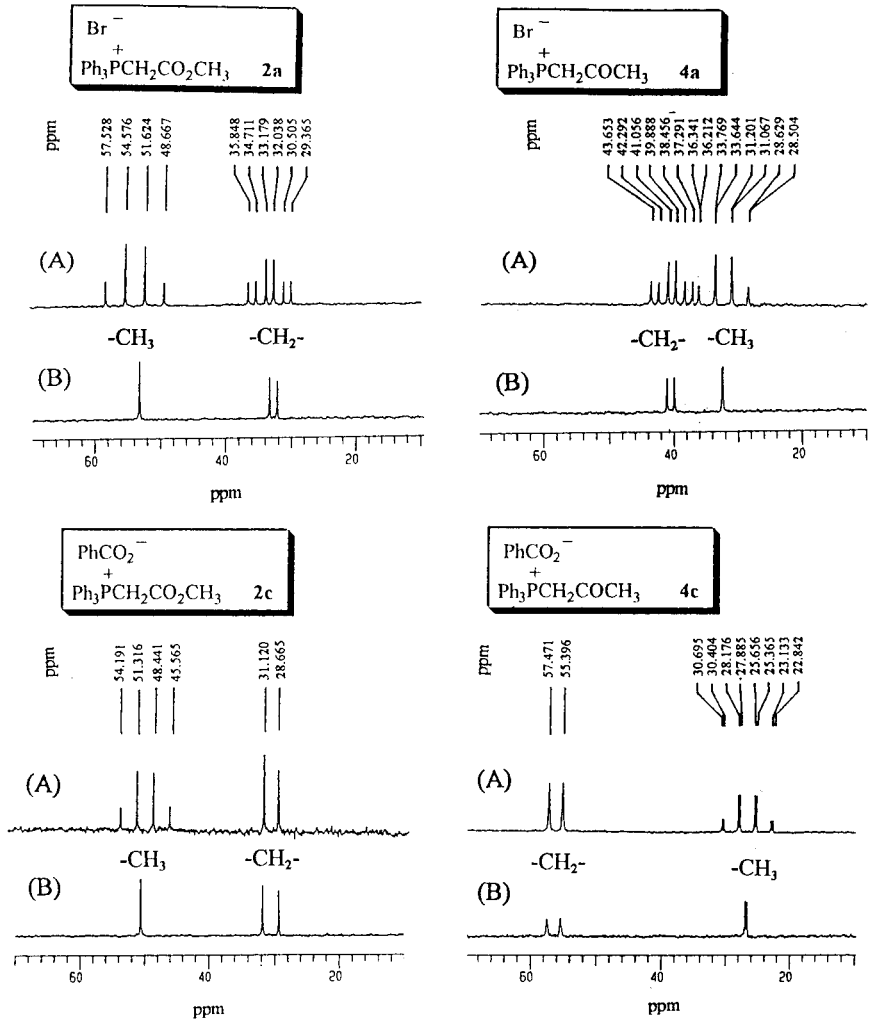


Figure 2. The characteristic ^{13}C NMR signals for the phosphonium salts **2a**, **2c**, **4a** and **4c** (Top: proton-decoupled; Bottom: proton-coupled).

acetates (i.e. **2b** and **4b**), benzoates (i.e. **2c** and **4c**) or formates (i.e. **2d** and **4d**), they underwent Wittig reaction with aldehyde **8** within 0.5 h in excellent yields (Entries 2–4; 9–11). Interestingly, the phosphonium chloroacetate (i.e. **2e** and **4e**) needed longer time (4.5–7 h) to give α,β-unsaturated carbonyl compounds in good yields (Entries 5 and 12). Furthermore, when the counteranion was trifluoroacetate (i.e. **2f**), its reactivity with aldehyde was sluggish. It took 24 h at rt to give α,β-unsaturated ester **9a** in 30% yield and 49% of the aldehyde was recovered (Entry 6). The results in Table 1 indicate that the reactivity of the phosphonium salts in Wittig reaction is counteranion-dependent.

We then turned our interest to study the reactivity of the triphenylarsonium analogues and their results are shown in Table 2. The results also indicate that the structures of the counteranion profoundly affect the reactivity of the arsonium salts in Wittig reaction.

In other words, the onium benzoates, formates, and acetates show excellent reactivity with aldehyde, whereas the onium bromides and tosylataes are not reactive for the same reaction. It is worthy to mention that the Wittig reaction rate from the phosphonium carboxylate (i.e. **2b**, **2c**, or **2d**) is faster than that from the corresponding phosphonium ylide **2a**. It needs 1.5 h to complete the reaction with 3-phenylpropanal (**8**) for the ylide.[4e] Therefore, we have disclosed the new possibility to carry out the Wittig reaction from the phosphonium salts (or arsonium salts) instead of the corresponding ylides. From the present study, we can arrange the order of the reactivity for the onium salts according to their counteranions as follows: p-TsO^-, $Br^- \ll CF_3CO_2^- \ll ClCH_2CO_2^- < PhCO_2^-$, HCO_2^-, $MeCO_2^-$.

The splitting patterns of the proton-coupled ^{13}C NMR in the phosphonium and arsonium salts

In order to correlate the structures of the triphenylphosphonium (or arsonium) salts to their reactivity with aldehyde as described in Tables 1 and 2, their ^1H NMR, broad band-decoupled ^{13}C NMR and off-resonance decoupled (i.e. proton-coupled) ^{13}C NMR spectra were taken in $CDCl_3$ at rt. We found that the proton-coupled splitting patterns of the α-carbon (i.e. the carbon next to carbonyl group) signal provided the most useful information as shown in Table 1. The α-carbon splitting patterns for those poor reactive phosphonium salts consistently appeared as the triplet of doublet where it was coupled with both of the adjacent proton and phosphorus nuclei (Entries, 1, 5–8, 12, Table 1). For

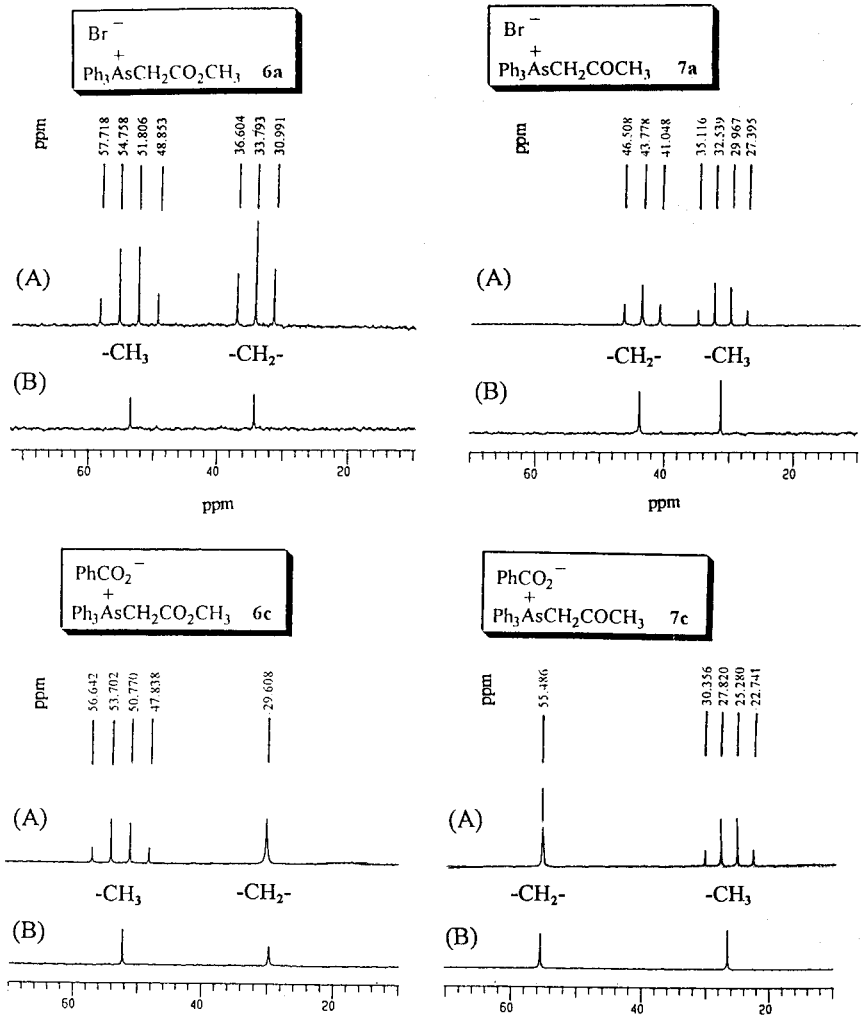


Figure 3. The characteristic ^{13}C NMR signals for the arsonium salts **6a**, **6c**, **7a** and **7c** (Top: Proton-decoupled; Bottom: proton-coupled).

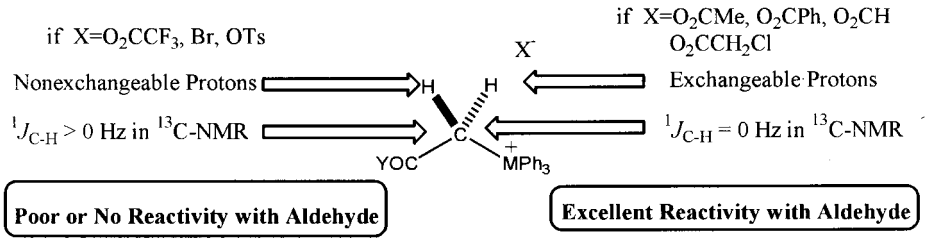


Figure 4. The reactivity of the onium salts with aldehyde is counteranion-dependent (Y=Me, OMe; M=P, As).

example, the triphenylphosphonium bromides were inert to the aldehyde. Therefore, the α-carbon splitting pattern for the methoxycarbonylmethyltriphenylphosphonium bromide (**2a**) appeared as a triplet of doublet (δ 32.7 ppm; $^1J_{H-C}$=133.7 Hz, $^1J_{P-C}$=57.0 Hz) and the acetonyltriphenylphosphonium bromide (**4a**) also appeared as a triplet of doublet (δ 40.6 ppm; $^1J_{H-C}$=130.0 Hz, $^1J_{P-C}$=58.4 Hz) (Fig. 2).

On the other hand, the α-carbon splitting patterns for the phosphonium salts having excellent reactivity in the Wittig reaction appeared as a doublet only. It is because the α-carbon is coupled with the adjacent phosphorus but not with hydrogen nuclei (Entries 2–4, 9–11, Table 1). For example, those phosphonium benzoates (**2c**) and (**4c**) showed excellent reactivity with aldehyde and their α-carbons appeared as a doublet (Entries 3 and 10, Table 1; Fig. 2). Therefore, the disappearance of the H–C coupling (i.e. $^1J_{H-C}$=0 Hz) for the α-carbon is an important indication to the high reactivity of the phosphonium salts in the Wittig reaction. Oppositely, those phosphonium salts with distinct H–C coupling (i.e. $^1J_{H-C}$>0 Hz) will have poor reactivity with the aldehyde.

Since the nuclear spin quantum number of arsine is zero, it does not couple with the neighboring nuclei. Therefore, the off-resonance decoupled splitting pattern for the triphenylarsonium salts should be simpler than that of the triphenylphosphonium analogues. For example, the α-carbon for the methoxycarbonylmethyltriphenylarsonium bromide (**6a**) and the acetonyltriphenylarsonium bromide (**7a**) appeared as triplets at δ 33.8 ppm ($^1J_{H-C}$=141.1 Hz) and δ 40.2 ppm ($^1J_{H-C}$=136.5 Hz), respectively. Both compounds had distinct $^1J_{H-C}$ values so that they had no reactivity with aldehyde (Entries 1 and 5, Table 2; Fig. 3). On the other hand, the α-carbon splitting patterns for the triphenylarsonium benzoates **6c** and **7c** appeared as singlets at δ 29.7 ppm ($^1J_{H-C}$=0 Hz) and δ 55.5 ppm ($^1J_{H-C}$=0 Hz), respectively. They should have excellent reactivity with aldehyde as expected (Entries 3 and 7, Table 2; Fig. 3). Therefore, the empirical rule to predict the reactivity of the triphenylphosphonium salts based on the $^1J_{H-C}$ values can also be applied to the corresponding triphenylarsonium salts (Table 2 and Fig. 4). The reason for the absence of the H–C coupling in the reactive phosphonium salts can be rationalized by the example of triphenylphosphonium acetates **2b** as shown in Fig. 5. The α-methylene group of compound **2b** is quite acidic so that the intramolecular proton exchange rate between the α-methylene group and acetate is too fast to be differentiated by NMR. This exchange process gives a transient intermediate (i.e. ylide and acetic acid) which can subsequently undergo Wittig reaction with aldehyde (Fig. 5). The acetic acid formed in the transient intermediate will serve as a catalyst to accelerate the Wittig reaction (Fig. 5).[4e] Therefore, the reaction rate of the phosphonium acetate with aldehyde should be faster than the reaction involving the phosphonium ylide only. We have reported that the α-methine proton of the stable phosphonium ylide could be exchanged rapidly with the trace amount of the proton source in the reaction media.[5f] In Fig. 5, both the acetic acid and phosphonium ylide are formed as transient intermediates. Therefore, the acetic acid can exchange rapidly with the α-methine proton of the phosphonium ylide (Fig. 5). This

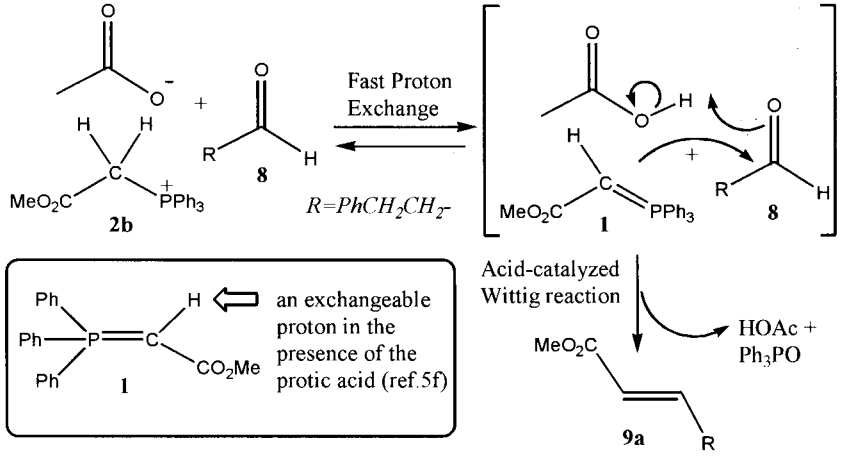


Figure 5. Proposed mechanism for the reaction of the phosphonium acetate with aldehyde.

exchange process is responsible to the disappearance of the C–H coupling in the ^{13}C NMR. On the other hand, NMR did not detect the intramolecular proton exchange between α-methylene group and bromide of the triphenylphosphonium bromide **2a**. Apparently, the exchange process is determined by the Bronsted basicity of the counteranion. Since the bromide is a weak Bronsted base, the intramolecular proton transfer in the phosphonium bromide is not possible. Therefore, it is not reactive in the Wittig reaction. The Bronsted basicity of the counteranion decreases in the following order: $CH_3CO_2^- > PhCO_2^- > HCO_2^- > ClCH_2CO_2^- > CF_3CO_2^- > OTs^- > Br^-$.[6] The results in Tables 1 and 2 indicate that the triphenylphosphonium (or arsonium) salts are effective in the Wittig reaction only when the basicities of their counteranions are ranged between formate and chloroacetate. In other words, the conjugated acid's p*K*a of the counteranion in triphenylphosphonium (or arsonium) salts should not be lower than 4 in order to have good reactivity with aldehyde.

The pathway II in Scheme 1 is an effective but expensive process to prepare the reactive phosphonium salts. Therefore, to develop an economic process is needed. We carried out the in situ anion exchange from the triphenylphosphonium bromide with NaOAc in acetonitrile although it was an heterogeneous process. The Wittig reaction products were isolated in high yield when triphenylphosphonium bromides reacted with aldehyde in the presence of 1.2 mol equiv. of NaOAc in refluxing acetonitrile for 2 h. A mixture of *E*- and *Z*-isomers was obtained and the *E*-isomer was the major product under this reaction condition. They were separable by silica gel column chromatography. This reaction condition was applied to prepare several conjugated carbonyl compounds in high yields as shown in Eq. (1).

$Ph_3P^+CH_2X\ Br^-$ + $Ph(CH_2)_2CHO$

X=CO_2Me **2a**; X=CO_2Bu-*t* **2h**; X=CN **2i**; X=COMe **4a**

8

1.2 equiv NaOAc, MeCN, reflux, 2 h → $Ph(CH_2)_2CH{=}CHX$ (1)

X=CO_2Me	**9a**	91% (*E*/*Z*=88/12)
X=CO_2Bu-*t*	**9h**	87% (E/Z=93/7)
X=CN	**9i**	84% (*E*/*Z*=70/30)
X=COMe	**9a'**	85% (*E*/*Z*=95/5)

Ph_3P + $BrCH_2CO_2Me$ + $Ph(CH_2)_2CHO$

8

1.2 equiv NaOAc, MeCN, reflux, 16 h → $Ph(CH_2)_2CH{=}CHCO_2Me$ (2)

9a 89% (*E*/*Z*=91/9)

$Ph_3As^+CH_2CO_2Me\ Br^-$ + $Ph(CH_2)_2CHO$

6a **8**

1.2 equiv NaOAc, MeCN, reflux, 4 h → $Ph(CH_2)_2CH{=}CHCO_2Me$ (3)

9a 87% (*E*/*Z*=97/3)

There are some important features for this anion exchange approach. We are able to carry out the Wittig reaction by mixing all of four reactants in the same flask to give the desired product in excellent yield as shown in Eq. (2). The phosphonium bromide formation, the anion exchange process and the reaction of the phosphonium acetate with aldehyde occur sequentially in the same pot. We have mentioned above that it is difficult for us to prepare $Ph_3As{=}CHCO_2Me$. Since our anion exchange process avoids using ylide directly, we can easily get rid of the above difficulty by reaction of the triphenylarsonium bromide **6a** with aldehyde **8** in the presence of sodium acetate as shown in Eq. (3). The reaction yield is excellent. The disadvantage of this anion exchange approach are: (1) it needs heating and longer reaction time; (2) both *E*- and *Z*-isomers can be obtained from Eqs. (1)–(3) while only *E*-isomer can be obtained from the corresponding phosphonium carboxylate as shown in Tables 1 and 2.

Conclusion

In summary, the proton-coupled ^{13}C NMR technique is an important tool in the prediction of the reactivity of the triphenylphosphonium (or arsonium) salts with aldehyde. Only those salts with fast intramolecular proton exchange process between the activated methylene group and the counteranion (i.e. $^1J_{C-H}$=0 Hz) can react with aldehyde to give α,β-unsaturated carbonyl compounds in good yields. From the present study, we found that the p*K*a of the conjugated acid of the counteranion could not be lower than 2.87.

Experimental

All reactions were carried out under nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Melting points were determined by using a Thomas–Hoover melting point apparatus and were uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance APX-400 and a Varian Gemini-200 spectrometers, and chemical shifts were given in ppm downfield from tetramethylsilane (TMS). IR spectra were taken with a Perkin–Elmer 682 spectrophotometer and only noteworthy absorption was listed. Mass spectra were measured on a VG-Trio-2000GC/MS spectrometer by electronic impact at 70 eV (unless otherwise indicated). High Resolution Mass Spectroscopy (HRMS) was measured on a JEOL JMS-HX 110 (National Hsing-Hua University) or VG-11–250J (Academia Sinica) Mass Spectrometer. The elemental analyses were measured on Heraeus NCH-RAPID and Perkin-Elmer 2400 CHN analyzer.

General procedure to prepare the phosphonium salts by the addition of protic acid to the phosphonium ylide (Pathway I)

To a stirring solution of the phosphonium ylide **1** (454.7 mg, 1.36 mmol) in 4 mL of anhydrous CH_2Cl_2 was added a solution of acetic acid (81.7 mg, 1.36 mmol) in 1 mL of anhydrous CH_2Cl_2 at rt under nitrogen. The reaction mixture was stirred for 5 min and concentrated in vacuo to give 536 mg of phosphonium acetate **2b** as white solid in quantitative yield.

General procedure to prepare the phosphonium salts by the reaction of the phosphonium bromide with silver salt (Pathway II)

To a stirring solution of the phosphonium bromide **2a** (265.8 mg, 0.64 mmol) in 5 mL of anhydrous CH_2Cl_2 was added silver acetate (111.8 mg, 0.67 mmol) in one portion at rt under nitrogen. The reaction mixture was stirred for 5 min and was centrifuged to precipitate the silver bromide. The solution was filtered and concentrated to give 251 mg of phosphonium acetate **2b** as white solid in quantitative yield.

Methoxycarbonylmethyltriphenylphosphonium bromide (2a).[7] White solid; mp 161–162°C; ^{1}H NMR ($CDCl_3$) δ 3.59 (s, 3H, $-CH_3$), 5.64 (d, J=13.4 Hz, 2H, $-CH_2-$), 7.65–7.94 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 32.7 (d, $^1J_{P-C}$=57.0 Hz), 53.2, 117.5 (d, $^1J_{P-C}$=88.8 Hz), 130.0 (d, $^3J_{P-C}$=13.1 Hz), 133.6 (d, $^2J_{P-C}$=10.9 Hz), 135.0, 164.7; IR (KBr) 1724, 1586, 1429 cm^{-1}; MS *m/z* (relative intensity): 334 (M^+-HBr, 24), 277 (67), 183 (100).

Methoxycarbonylmethyltriphenylphosphonium acetate (2b). White solid; mp 128–130°C; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3H, $-CH_3$), 3.52 (s, 3H, $-CH_3$), 6.43 (s, 2H, $-CH_2-$), 7.50–7.74 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 22.2, 30.4 (d, $^1J_{P-C}$=105.8 Hz), 50.8, 124.8 (d, $^1J_{P-C}$=89.2 Hz), 129.1 (d, $^3J_{P-C}$=12.4 Hz), 132.8, 133.1 (d, $^2J_{P-C}$=10.3 Hz), 169.9, 175.4; IR (KBr) 1724, 1613, 1457 cm^{-1}; MS *m/z* (relative intensity): 334 ($M^+-CH_3CO_2H$, 51), 333 (100), 152 (69); Anal. Calcd for $C_{23}H_{23}O_4P$: C, 70.04; H, 5.88. Found: C, 70.18; H, 5.89.

Methoxycarbonylmethyltriphenylphosphonium benzoate (2c). White solid; mp 155–158°C; ^{1}H NMR ($CDCl_3$) δ 3.53 (s, 3H, $-CH_3$), 4.54 (br, 2H, $-CH_2-$), 7.42–8.08 (m, 20H, $-CH_2-$ and Ph); ^{13}C NMR ($CDCl_3$) δ 29.9 (d, $^1J_{P-C}$=124.2 Hz), 49.9, 127.1 (d, $^1J_{P-C}$=54.6 Hz), 128.7 (d, $^3J_{P-C}$=12.4 Hz), 132.0, 133.0 (d, $^2J_{P-C}$=10.2 Hz), 169.8, 171.5; IR (KBr) 1726, 1631, 1442, 1347 cm^{-1}; MS *m/z* (relative intensity): 334 (M^+-PhCO_2H, 40), 333 (89), 183 (100); Anal. Calcd for $C_{28}H_{25}O_4P$: C, 73.67; H, 5.52. Found: C, 73.38; H, 5.53.

Methoxycarbonylmethyltriphenylphosphonium formate (2d). White solid; mp 136–138°C; ^{1}H NMR ($CDCl_3$) δ 3.51 (s, 3H, $-CH_3$), 5.18 (s, 2H, $-CH_2-$), 7.50–7.73 (m, 15H, Ph), 8.51 (s, 1H, HCOO); ^{13}C NMR ($CDCl_3$) δ 30.1 (d, $^1J_{P-C}$=110.6 Hz), 50.4, 125.4 (d, $^1J_{P-C}$=91.0 Hz), 128.9 (d, $^3J_{P-C}$=12.4 Hz), 132.5, 132.9 (d, $^2J_{P-C}$=9.9 Hz), 166.5, 170.1 (d, J=8.5 Hz); IR (KBr) 1742, 1613, 1438 cm^{-1}; MS *m/z* (relative intensity): 334 (M^+-HCO_2H, 25), 277 (57), 152 (100); Anal. Calcd for $C_{22}H_{21}O_4P$: C, 69.47; H, 5.56. Found: C, 69.49; H, 5.70.

Methoxycarbonylmethyltriphenylphosphonium chloroacetate (2e). White solid; mp 103–106°C; ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 3H, $-CH_3$), 3.92 (s, 2H, $-CH_2-$), 6.12 (br, 2H, $-CH_2-$), 7.53–7.73 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 30.6 (d, $^1J_{P-C}$=84.6 Hz), 43.8, 51.8, 121.7 (d, $^1J_{P-C}$=89.8 Hz), 129.5 (d, $^3J_{P-C}$=12.7 Hz), 133.3 (d, $^2J_{P-C}$=10.3 Hz), 133.8, 167.8, 170.5; IR (KBr) 3050, 1738, 1618, 1436, 1346 cm^{-1}; MS *m/z* (relative intensity): 335 ($M^+-ClCH_2CO_2$, 100), 334 ($M^+-ClCH_2CO_2H$, 6), 277 (32), 183 (9); Anal. Calcd for $C_{23}H_{22}O_4ClP$: C, 64.42; H, 5.17. Found: C, 64.36; H, 5.20.

Methoxycarbonylmethyltriphenylphosphonium trifluoroacatate (2f). White solid; mp 117–119°C; ^{1}H NMR ($CDCl_3$) δ 3.59 (s, 3H, $-CH_3$), 5.34 (d, J=13.8 Hz, 2H, $-CH_2-$), 7.60–7.85 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 31.2 (d, $^1J_{P-C}$=58.0 Hz), 53.3, 117.9 (q, J_{C-F}=89.0 Hz), 130.2 (d, $^3J_{P-C}$=13.0 Hz), 133.0 (d, $^1J_{P-C}$=11.0 Hz), 133.7 (d, $^2J_{P-C}$=11.0 Hz), 135.1, 160.7 (q, J_{C-F}=33.0 Hz), 165.3; IR (KBr) 1733, 1682, 1461, 1374 cm^{-1}; MS *m/z* (relative intensity): 334 ($M^+-CF_3CO_2H$, 0.3), 277 (100), 183 (18); Anal. Calcd for $C_{23}H_{20}O_4F_3P$: C, 61.61; H, 4.50. Found: C, 61.56; H, 4.59.

Methoxycarbonylmethyltriphenylphosphonium *p*-toluenesulfonate (2g). White solid; mp 162–164°C; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3H, $-CH_3$), 3.53 (s, 3H, $-CH_3$), 5.18 (d, J=13.6 Hz, 2H, $-CH_2-$), 7.02 (d, J=8 Hz, 2H, Ph), 7.61–7.85 (m, 17H, Ph); ^{13}C NMR ($CDCl_3$) δ 21.1, 31.3 (d, $^1J_{P-C}$=58.1 Hz), 53.2, 117.9 (d, $^1J_{P-C}$=88.8 Hz), 126.0, 128.0, 130.1 (d, $^3J_{P-C}$=13.1 Hz), 133.7 (d, $^2J_{P-C}$=10.6 Hz), 135.0, 138.2, 144.3, 165.2; IR (KBr) 3059, 1719, 1603, 1480, 1438 cm^{-1}; MS *m/z* (relative intensity): 334 ($M^+-CH_3C_6H_4SO_3H$, 0.3), 277 (95), 154 (98), 78 (100); Anal. Calcd for $C_{28}H_{27}O_5PS$: C, 66.39; H, 5.37. Found: C, 66.30; H, 5.32.

Acetonyltriphenylphosphonium bromide (4a). White solid; mp 221–223°C; ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3H, $-CH_3$), 5.96 (d, J=11.3 Hz, 2H, $-CH_2-$), 7.53–7.81 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 32.5 (d, $^3J_{P-C}$=6.5 Hz), 40.6 (d, $^1J_{P-C}$=58.4 Hz), 118.4 (d, $^1J_{P-C}$=88.4 Hz), 129.9 (d, $^3J_{P-C}$=12.9 Hz), 133.7 (d, $^2J_{P-C}$=10.7 Hz), 134.5, 200.6 (d, J=6.9 Hz); IR (KBr) 3050, 1715, 1618, 1443 cm^{-1}; MS *m/z* (relative intensity): 319 (M^+-Br, 45), 318 (M^+-HBr, 100), 183 (23); Anal. Calcd for $C_{21}H_{20}OPBr$: C, 63.17; H, 5.05. Found: C, 63.15; H, 5.10.

Acetonyltriphenylphosphonium acetate (4b). White solid; mp 135–138°C; ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3H, $-CH_3$), 2.11 (s, 3H, $-CH_3$), 7.46–7.65 (m, 17H, $-CH_2-$ and Ph); ^{13}C NMR ($CDCl_3$) δ 21.7, 26.8 (d, $^1J_{P-C}$=14.6 Hz), 56.2 (d, J=106 Hz), 125.8 (d, $^1J_{P-C}$=90.5 Hz), 128.9 (d, $^3J_{P-C}$=12.3 Hz), 132.4, 133.0 (d, $^2J_{P-C}$=10.2 Hz), 174.4, 190.0; IR (KBr) 3059, 1696, 1484 cm^{-1}; MS *m/z* (relative intensity): 319 (M^+-OAc, 100), 318 (M^+-HOAc, 25), 185 (12); Anal. Calcd for $C_{23}H_{23}O_3P$: C, 73.00; H, 6.13. Found: C, 73.03; H, 6.07.

Acetonyltriphenylphosphonium benzoate (4c). White solid; mp 136–137°C; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H, $-CH_3$), 7.35–7.69 (m, 20H, $-CH_2-$ and Ph), 8.04–8.06 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$) δ 26.8 (d, $^1J_{P-C}$=14.4 Hz), 56.5 (d, J=105.6 Hz), 125.5 (d, $^1J_{P-C}$=90.0 Hz), 127.7, 128.9 (d, $^3J_{P-C}$=12.2 Hz), 129.6, 131.4, 132.4, 133.1 (d, $^2J_{P-C}$=10.0 Hz), 169.4, 190.1; IR (KBr) 3050, 1701, 1521, 1263 cm^{-1}; MS *m/z* (relative intensity): 319 (M^+-PhCO_2, 5), 318 (M^+-PhCO_2H, 24), 303 (100); Anal. Calcd for $C_{28}H_{25}O_3P$: C, 76.35; H, 5.72. Found: C, 76.26; H, 5.78.

Acetonyltriphenylphosphonium formate (4d). White solid; mp 152–154°C; ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3H, CH_3), 7.49–7.66 (m, 17H, $-CH_2-$ and Ph), 8.17 (s, 1H, HCOO); ^{13}C NMR ($CDCl_3$) δ 26.5 (d, $^1J_{P-C}$=14.2 Hz), 57.3 (d, J=104.2 Hz), 125.2 (d, $^1J_{P-C}$=90.6 Hz), 129.0 (d, $^3J_{P-C}$=12.5 Hz), 132.6, 133.0 (d, $^2J_{P-C}$=10.0 Hz), 165.3, 189.1; IR (KBr) 1724, 1609, 1438, 1351 cm^{-1}; MS *m/z* (relative intensity): 319 (M^+-HCO_2, 4), 318 (M^+-HCO_2H, 19), 303 (100); Anal. Calcd for $C_{22}H_{21}O_3P$: C, 72.52; H, 5.81. Found: C, 72.57; H, 5.92.

Acetonyltriphenylphosphonium chloroacetate (4e). White solid; mp 94–96°C; ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3H, $-CH_3$), 3.93 (s, 2H, $-CH_2-$), 6.92 (br, 2H, $-CH_2-$), 7.53–7.68 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 25.1 (dd, J=13.3 Hz, J=28.1 Hz), 40.3, 59.7 (d, $^1J_{P-C}$=99.8 Hz), 122.9 (d, $^1J_{P-C}$=91.3 Hz), 128.9 (d, $^3J_{P-C}$=12.6 Hz), 132.6 (d, $^2J_{P-C}$=10.5 Hz), 132.8, 169.9, 187.1; IR (KBr) 3059, 1715, 1609, 1438 cm^{-1}; MS *m/z* (relative intensity): 319 ($M^+-ClCH_2CO_2$, 100), 318 ($M^+-ClCH_2CO_2H$, 14), 303 (13), 183 (10); Anal. Calcd for $C_{23}H_{22}O_3ClP$: C, 66.91; H, 5.37. Found: C, 66.99; H, 5.39.

Acetonyltriphenylphosphonium *p*-toluenesulfonate (4g). White solid; mp 163–165°C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3H, $-CH_3$), 2.50 (s, 3H, $-CH_3$), 5.59 (d, J=11.5 Hz, 2H, $-CH_2-$), 7.06 (d, J=3.9 Hz, 2H, Ph), 7.54–7.79 (m, 17H, Ph); ^{13}C NMR ($CDCl_3$) δ 21.1, 31.9 (d, $^3J_{P-C}$=6.5 Hz), 39.0 (d, $^1J_{P-C}$=59.5 Hz), 118.5 (d, $^1J_{P-C}$=88.6 Hz), 125.8, 128.2, 129.5, 129.9 (d, $^3J_{P-C}$=13.2 Hz), 133.6 (d, $^2J_{P-C}$=10.7 Hz), 134.4, 138.7, 143.6, 201.1 (d, J=6.7 Hz); IR (KBr) 1719, 1443, 1263 cm^{-1}; MS *m/z* (relative intensity): 319 (M^+-OTs, 5), 318 (M^+-TsOH, 23), 303 (100); Anal. Calcd for $C_{27}H_{27}O_4PS$: C, 68.56; H, 5.55. Found: C, 68.51; H, 5.60.

Methoxycarbonylmethyltriphenylarsonium bromide (6a). White solid; mp 179–180°C; ^{1}H NMR ($CDCl_3$) δ 3.51 (s, 3H, $-CH_3$), 5.41 (s, 2H, $-CH_2-$), 7.56–7.76 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 34.2, 53.5, 121.2, 130.7, 133.0, 134.1, 166.2; IR (KBr) 1721, 1437, 1317 cm^{-1}; MS *m/z* (relative intensity): 378 (M^+-HBr, 0.13), 306 (21), 152 (100). Anal. Calcd for $C_{21}H_{20}O_2AsBr$: C, 54.93; H, 4.39. Found: C, 54.89; H, 4.34.

Methoxycarbonylmethyltriphenylarsonium acetate (6b). White solid; mp 136–138°C; ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 3H, $-CH_3$), 3.53 (s, 3H, $-OCH_3$), 6.81 (s, 2H, $-CH_2-$), 7.53–7.70 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 23.1, 32.1, 51.9, 124.4, 130.0, 132.4, 132.5, 133.0, 168.8, 175.9; IR (KBr) 3059, 1728, 1599, 1484, 1434 cm^{-1}; MS *m/z* (relative intensity): 306 (17), 227 (20), 152 (100). Anal. Calcd for $C_{23}H_{23}O_4As$: C, 63.02; H, 5.29. Found: C, 63.39; H, 5.25.

Methoxycarbonylmethyltriphenylarsonium benzoate (6c). White solid; mp 104–107°C; ^{1}H NMR ($CDCl_3$) δ 3.46 (s, 3H, $-CH_3$), 7.22–7.98 (m, 22H, $-CH_2-$ and Ph); ^{13}C NMR ($CDCl_3$) δ 29.7, 52.2, 123.4, 127.0, 129.4, 129.6, 130.1, 132.2, 133.2, 136.7, 169.3, 171.2; IR (KBr) 3050, 1728, 1595, 1443, 1374 cm^{-1}; MS *m/z* (relative intensity): 378 (M^+-PhCO_2H, 5), 306 (14), 152 (100). HRMS Calcd for (M^+-PhCO_2H) $C_{21}H_{19}O_2As$: 378.0602. Found: 378.0601.

Methoxycarbonylmethyltriphenylarsonium trifluoroacetate (6f). White solid; mp 117–120°C; ^{1}H NMR ($CDCl_3$) δ 3.61 (s, 3H, $-CH_3$), 5.28 (s, 2H, $-CH_2-$), 7.65–7.78 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 32.2, 53.4, 121.2, 130.6, 132.7, 134.1, 160.6 (q, J_{C-F}=32.6 Hz), 166.4; IR (KBr) 1738, 1687, 1447, 1263 cm^{-1}; MS *m/z* (relative intensity): 379 (M^+-CF_3COO, 0.03), 306 (34), 152 (100); Anal. Calcd for $C_{23}H_{20}O_4F_3As$: C, 56.11; H, 4.09. Found: C, 56.11; H, 4.15.

Acetonyltriphenylarsonium bromide (7a).[8] White solid; mp 169–170°C; ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 3H, $-CH_3$), 6.01 (s, 2H, $-CH_2-$), 7.51–7.75 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 31.3, 43.8, 121.6, 130.2, 132.6, 133.4, 201.6; IR (KBr) 3032, 2820. 1710, 1438, 1355 cm^{-1}; MS *m/z* (relative intensity): 364 (100), 362 (M^+-HBr, 12), 229 (21), 152 (24).

Acetonyltriphenylarsonium acetate (7b). White solid; mp 104–106°C; ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 3H, $-CH_3$), 2.19 (s, 3H, $-CH_3$), 6.83 (s, 2H, $-CH_2-$), 7.51–7.67 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 22.3, 26.1, 57.0, 126.9, 129.6, 132.2, 132.4, 175.1, 189.0; IR (KBr) 3050, 1710, 1516, 1438, 1268 cm^{-1}; MS *m/z* (relative intensity): 363 (M^+-OAc, 100), 362 (M^+-HOAc, 11), 229 (17), 152 (23); Anal. Calcd for $C_{23}H_{23}O_3As$: C, 65.41; H, 5.49. Found: C, 65.20; H, 5.60.

Acetonyltriphenylarsonium benzoate (7c). White solid; mp 108–110°C; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3H, $-CH_3$), 7.29–8.03 (m, 20H, $-CH_2-$ and Ph), 8.50 (s, 2H, Ph); ^{13}C NMR ($CDCl_3$) δ 26.5, 55.5, 126.0, 127.4, 129.2, 129.5, 129.6, 130.5, 132.3, 170.3, 190.5; IR (KBr) 3059, 1710, 1599, 1438, 1369 cm^{-1}; MS *m/z* (relative intensity): 362 (M^+-PhCO_2H, 1.1), 306 (27), 152 (100); Anal. Calcd for $C_{28}H_{25}O_3As$: C, 69.42; H, 5.20. Found: C, 69.35; H, 5.33.

Acetonyltriphenylarsonium formate (7d). White solid; mp 118–120°C; ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 3H, $-CH_3$), 7.49–7.68 (m, 17H, $-CH_2-$ and Ph), 8.42 (1H, HCO_2); ^{13}C NMR ($CDCl_3$) δ 26.5, 56.0, 126.2, 129.8, 132.4, 166.5, 189.6; IR (KBr) 3050, 1710, 1599, 1512, 1438 cm^{-1}; MS *m/z* (relative intensity): 363 ($M^+-HCO_2^-$, 100), 362 (M^+-HCO_2H, 9), 347 (11), 229 (13), 152 (18); Anal. Calcd for $C_{22}H_{21}O_3As$: C, 64.71; H, 5.18. Found: C, 64.69; H, 5.18.

Acetonyltriphenylarsonium trifluoroacetate (7f). White

solid; mp 138–139°C; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H, $-CH_3$), 5.67 (s, 2H, $-CH_2-$), 7.60–7.74 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 30.5, 42.2, 121.8, 130.4, 132.6, 133.6, 160.8, 201.9; IR (KBr) 1682, 1466, 1374 cm^{-1}; MS *m/z* (relative intensity): 362 ($M^+-CF_3CO_2H$, 3.3), 227 (38), 152 (100); Anal. Calcd for $C_{23}H_{20}O_3F_3As$: C, 58.00; H, 4.23. Found: C, 58.22; H, 4.45.

General procedure of the Wittig reaction from the triphenylphosphonium carboxylate with aldehyde

The solution of phosphonium acetate **2b** (394.4 mg, 1.0 mmol) and 3-phenylpropanal (**8**) (134.1 mg, 1.0 mmol) in 5 mL of anhydrous CH_2Cl_2 was stirred at rt for 30 min. The solution was concentrated and chromatographed to give 174.9 mg of Wittig reaction product **9a**–**E** (0.92 mmol) as colorless oil in 92% yield.

General procedure of the Wittig reaction from the triphenylphosphonium bromide with aldehyde in the presence of sodium acetate

A mixture of the phosphonium bromide **2a** (415.3 mg, 1.0 mmol), 3-phenylpropanal (**8**) (134.2 mg, 1.0 mmol) and sodium acetate (98.4 mg, 1.2 mmol) in 5 mL of anhydrous acetonitrile was refluxed under nitrogen for 2 h. The solution was concentrated and chromatographed to give 152.1 mg of **9a-*E*** (0.80 mmol) and 20.9 mg of **9a-*Z*** (0.11 mmol) in 91% yield.

General procedure of the Wittig reaction from triphenylphosphine, methyl bromoacetate, 3-phenylpropanal (8) in the presence of sodium acetate

A mixture of triphenylphosphine (262.3 mg, 1.0 mmol), methyl bromoacetate (153.0 mg, 1 mmol), 3-phenylpropanal (**8**) (134.1 mg, 1 mmol) and sodium acetate (98.4 mg, 1.2 mmol) in 5 mL of anhydrous acetonitrile was refluxed under nitrogen for 16 h. The reaction mixture was concentrated and chromatographed to give 154.0 mg of **9a-*E*** (0.81 mmol) and 15.2 mg of **9a-*Z*** (0.08 mmol) in 89% yield.

Wittig reaction from the triphenylarsonium bromide with aldehyde in the presence of sodium acetate

To a stirring solution of the arsonium bromide **6a** (459.2 mg, 1.0 mmol), 3-phenylpropanal (**8**) (134.2 mg, 1.0 mmol) in 5 mL of anhydrous acetonitrile was added sodium acetate (98.4 mg, 1.2 mmol). The mixture was refluxed under nitrogen for 4 h. The solution was concentrated and chromatographed to give 159.7 mg of **9a-*E*** (0.84 mmol) and 5.7 mg of **9a-*Z*** (0.03 mmol) in 87% yield.

(*E*)-5-phenyl-2-pentenoic acid methyl ester (9a-*E*). ^{1}H NMR ($CDCl_3$) δ 2.49–2.55 (m, 2H, $-CH_2-$), 2.75–2.79 (m, 2H, $-CH_2-$), 3.71 (s, 3H, $-CH_3$), 5.84 (d, J=7.8 Hz, 1H, –CH=CH–), 6.97–7.04 (m, 1H, –CH=CH–), 7.16–7.31 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 33.8, 34.3, 51.4, 121.4, 126.1, 128.3, 128.4, 140.7, 148.3, 166.9; IR (KBr) 2940, 1733, 1659, 1438, 1318 cm^{-1}; MS *m/z* (relative intensity): 190 (M^+, 2.0), 130 (15), 91 (100); Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.71; H, 7.55.

(*Z*)-5-phenyl-2-pentenoic acid methyl ester (9a-*Z*). ^{1}H NMR ($CDCl_3$) δ 2.74–2.78 (m, 2H, $-CH_2-$), 2.95–2.99 (m, 2H, $-CH_2-$), 3.68 (s, 3H, $-CH_3$), 5.79–5.85 (m, 1H, –CH=CH–), 6.21–6.28 (m, 1H, –CH=CH–), 7.15–7.29 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 30.4, 35.0, 51.0, 119.9, 126.0, 128.3, 128.4, 141.1, 149.2, 166.7; IR (KBr) 2957, 1731, 1451, 1422 cm^{-1}; HRMS Calcd for $C_{12}H_{14}O_2$: 190.0944. Found: 190.0991.

(*E*)-2,2-dimethyl-7-phenyl-4-hepten-3-one (9h-*E*). ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 9H, $-(CH_3)_3$), 2.48–2.52 (m, 2H, $-CH_2-$), 2.75–2.78 (m, 2H, $-CH_2-$), 5.76–5.81 (m, 1H, –CH=CH–), 6.89–6.93 (m, 1H, –CH=CH–), 7.18–7.31 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 28.1, 33.8, 34.4, 80.1, 123.5, 126.1, 128.3, 128.4, 141.0, 146.8, 166.0; IR (KBr) 2967, 1715, 1655, 1457, 1369 cm^{-1}; MS *m/z* (relative intensity): 217 (M^++1, 10), 159 (26), 130 (18), 91 (100); Anal. Calcd for $C_{15}H_{20}O$: C, 77.55; H, 8.68. Found: C, 77.56; H, 8.64.

(*E*)-5-phenyl-2-pentenonitrile (9i-*E*). ^{1}H NMR ($CDCl_3$) δ 2.49–2.60 (m, 2H, $-CH_2-$), 2.73–2.80 (m, 2H, $-CH_2-$), 5.31(dd, J=16.2, 1.6 Hz, 1H, –CH=CH–), 6.65–6.80 (m, 1H, –CH=CH–), 7.13–7.35 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 33.9, 34.9, 100.4, 126.5, 128.1, 128.3, 154.7; IR (KBr) 3032, 2212, 1627, 1493 cm^{-1}; MS *m/z* (relative intensity): 157 (M^+, 18), 30 (4), 91 (100); Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05. Found: C, 84.00; H, 7.04.

(*Z*)-5-phenyl-2-pentenonitrile (9i-*Z*). ^{1}H NMR ($CDCl_3$) δ 2.49–2.60 (m, 2H, $-CH_2-$), 2.73–2.80 (m, 2H, $-CH_2-$), 5.27–5.36 (m, 1H, –CH=CH–), 6.45–6.50 (m, 1H, –CH=CH–) 7.13–7.35 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 33.2, 34.3, 100.2, 117.3, 126.5, 128.1, 128.3, 128.6, 153.8.

(*E*)-6-phenyl-3-hexen-2-one (9a′-*E*). ^{1}H NMR ($CDCl_3$) δ 2.23 (m, 3H, $-CH_3$), 2.49–2.60 (m, 2H, $-CH_2-$), 2.76–2.83 (m, 2H, $-CH_2-$), 6.04–6.13 (m, 1H, –CH=CH–), 6.75–6.89 (m, 1H, –CH=CH–), 7.16–7.35 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 27.0, 34.1, 34.4, 126.2, 128.1, 128.3, 128.5, 131.7, 198.5; IR (KBr) 3026, 1676, 1626, 1497, 1362 cm^{-1}; MS *m/z* (relative intensity): 174 (M^+, 5), 131 (13), 116 (46), 91(100); Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.69; H, 8.17.

(*Z*)-6-phenyl-3-hexen-2-one (9a′-*Z*). ^{1}H NMR ($CDCl_3$) δ 2.18 (m, 3H, $-CH_3$), 2.74–2.76 (m, 2H, $-CH_2-$), 2.91–2.97 (m, 2H, $-CH_2-$), 6.06–6.16 (m, 2H, –CH=CH–), 7.19–7.30 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 30.7, 31.5, 35.1, 126.0, 127.6, 128.3, 128.5, 141.1, 146.9, 199.1; IR (KBr) 2927, 1701, 1621, 1467, 1367 cm^{-1}; MS *m/z* (relative intensity): 174 (M^+, 12), 131 (40), 104 (21), 91 (100).

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