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A solvent-free facile synthesis of (*E*)-bis(phosphonium)ethylenes from organo-phosphines and $TfOCH_2CF_2H$ reagent

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ABSTRACT

(*E*)-Bis(phosphonium)ethylenes were synthesized from aryl-, alkyl-, and arylalkylphosphines under solvent-free conditions using $TfOCH_2CF_2H$ as reagent. The reaction allows for a convenient access to vinylenebis(trialkylphosphonium) salts in good to high yields.

Quaternary aryl and alkyl phosphonium salts have found a wide range of applications.[1] Some of them are the precursors of phosphonium ylides in the Wittig reactions.[2] Some can be utilized as phase transfer catalysts (PTC) and Lewis acids for a large number of chemical transformations.[3] Others provide excellent countercations to stabilize unusual and complex anions, providing very organic-soluble and easily crystallized salts.[1,4] The utilization of phosphonium cations to furnish ionic liquids as reaction media and materials is well in agreement with the principle of green chemistry.[5] To satisfy the needs of phosphonium salts from many research areas, the synthesis of various phosphonium-containing compounds is particularly important.[6,7]

Bis(phosphonium)ethylenes (e.g., $[Ar_3PCH{=}CHPAr_3]X_2$) bearing two phosphonium cations and a vinyl linkage are very intriguing intermediates and reagents.[8–11] The easy hydrolysis or alcoholysis of $[Ar_3PCH{=}CHPAr_3]X_2$ in the presence of bases, the nucleophilic vinylic substitution of the phosphonium group by *t*-Bu^- anion, the decisive application of bis(phosphonio)diaminoethene for the synthesis of 4,5-bis(dimethylamino)imidazolium species, and the incredible use of $[Ph_3PCH{=}CHPPh_3]Y_2$ ($Y = I^-$, Ph_4B^-) as fire-resistant additives indicated the rich chemistry of bis(phosphonium) ethylenes.[8a–d,h,i] Several approaches for the synthesis of these interesting salts from tertiary phosphines have been reported.[8–11] At the beginning, bis(triarylphosphonium)ethylenes $[Ar_3PCH{=}CHPAr_3]X_2$ ($X = Br^-$, Cl^-) with *E*-configuration were constructed by the reaction of Ar_3P with Ac_2O/HBr, AcBr, or AcCl.[8e–g] Later, (*E*)-vinylenebis(trialkylphosphonium) salt $[Bu_3PCH{=}CHPBu_3]\{[CH_3CO_2H]_2CH_3CO_2^-\}_2$ was verified to form in the reaction of Ac_2O and alcohol when Bu_3P was used as catalyst for the acetylation.[9] (*E*)-Bis(triphenylphosphonium)ethylene triflate ($[Ph_3PCH{=}CHPPh_3][OTf]_2$) was then produced by the reaction of diiodonium acetylene triflate and excess Ph_3P in wet CH_3CN at a low temperature (−35 °C).[10] Vinylenebis(alkylarylphosphonium) salts $[(E)\text{-}R^1R^2MePCH{=}CHPMeR^1R^2]I_2$ were eventually achieved by treatment of $(E)\text{-}R^1R^2PCH{=}CHPR^1R^2$ with MeI (1:2).[11] Although these methods can supply some bis(phosphonium)ethylenes, the disadvantages such as the narrow range of substrates, the use of air- and moisture-sensitive reagents, and the preparation of the tedious starting materials like diiodonium acetylene and $(E)\text{-}R^1R^2PCH{=}CHPR^1R^2$ restrain their applications.

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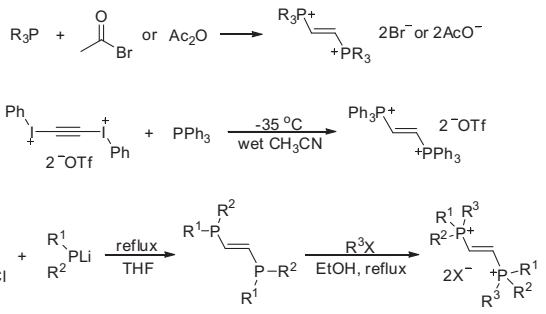
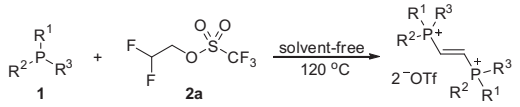
previous synthetic methods

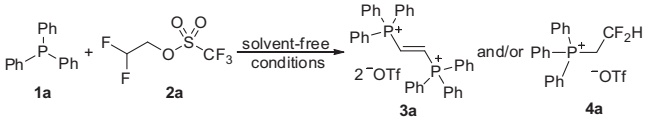


this work



Herein we report a concise synthesis of bis(phosphonium)ethylene salts from tertiary aryl and/or alkyl phosphines with the mild and bench-stable $TfOCH_2CF_2H$ reagent under solvent-free conditions. $TfOCH_2CF_2H$ is a powerful difluoroethylation reagent, which can incorporate the CH_2CF_2H group into bioactive molecules on the oxygen and nitrogen sites via S_N2 reactions.[12] However, the reactions of 2,2-difluoroethyl triflate with other types of nucleophiles are rarely known. It was reported that 2,2,2-trifluoroethyl triflate ($TfOCH_2CF_3$) reacting with triphenylphosphine (**1a**) in dry toluene at 100 °C for 2 days afforded $[Ph_3PCH_2CF_3][OTf]$ in 85% yield.[13] Nevertheless, treatment of $TfOCH_2CF_2H$ (**2a**) with PPh_3 (**1a**) at room temperature for 12 h under solvent-free condition, after crystallization, gave $[Ph_3PCH_2CF_2H][OTf]$ (**4a**) in 76% yield (entry 1, Table 1). Increasing the reaction temperature to 80 °C, it was surprising that, the reaction even with excess **2a** yielded a mixture of **3a** and **4a** (entry 2, Table 1). Further elevating the reaction temperature to 120 °C led to the formation of **3a** in 78% yield with only *E*-configuration (entry 3, Table 1). Using excess PPh_3 did not improve the yield of **3a** but promoted the availability of **2a** (entry 4, Table 1). The exact molecular structure of compound **3a** was determined by means of NMR spectroscopy and single crystal X-ray diffraction (Fig. 1).[14] $[Ph_3PCH_2CF_2H][OTf]$ (**4a**) has distinct

Table 1
The solvent-free reactions between Ph_3P and $TfOCH_2CF_2H$



Entry	Ratio[a]	Conditions (°C/h)	Yield[b] (%) **3a**[c] or **4a**
1	1:4.4	rt/12	76 (**4a**)[d]
2	1:1.2	80/12	80[e]
3	1:1.2	120/24	78 (**3a**)
4	2:1	120/15	50 (**3a**)

[a] The molar ratio of Ph_3P and HCF_2CH_2OTf.
[b] Isolated yield.
[c] Trace of fluorides was observed in the isolated products, which was determined by ^{19}F NMR (see SI).[15] Efforts to remove these byproducts by recrystallization failed. **3a** was obtained in *E*-configuration.
[d] 23% yield of **4a** was obtained when 1.2 equiv of HCF_2CH_2OTf was employed.
[e] Yield of the crude product. The molar ratio of **3a**/**4a** is 25:8, which was determined by NMR spectroscopy.

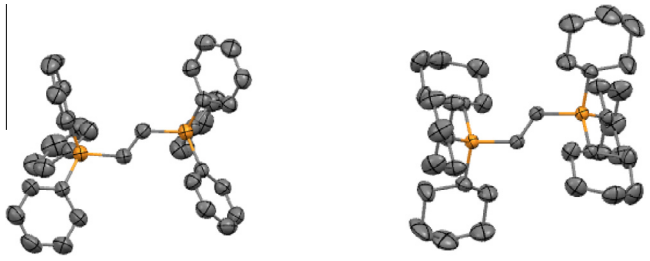
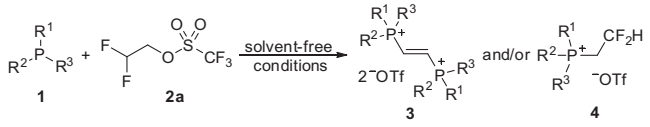


Figure 1. ORTEP diagrams of **3a** (left) and **3o** (right). Ellipsoids are shown at the 50% probability level. Hydrogens, anions, and solvents are omitted for clarity.

resonances at 6.62 ppm (tdt, J = 54.4, 7.7, 4.4 Hz) and 4.64 ppm (m) in ^1H NMR and −108.6 ppm (dm, J = 54.5 Hz) in ^{19}F NMR, while $[Ph_3PCH{=}CHPPh_3]X_2$ (**3a**) has a characteristic signal of 8.71 ppm (t, J = 20.7 Hz) in ^1H NMR, which can easily differentiate them.

To our delight, the reaction is also amenable to other triarylphosphines (entries 1–12, Table 2). Substrates either with electron-donating groups or with moderate electron-withdrawing groups on the phenyl rings are all transformed under the standard reaction conditions. As is the case of **1a**, the reaction temperature has great influence on the reaction (entries 1 and 2, 3 and 4, 16 and 17, Table 2). For instance, treatment of tris(*meta*-methylphenyl)phosphine (**1c**) with **2a** at room temperature for 12 h provided **4c** in 5% yield (entry 3, Table 2), and the same reaction mixture stirred at 120 °C for 6 h afforded **3c** in 80% yield (entry 4, Table 2). The position of substituents on phenyl rings of phosphines also severely impacts on the transformation. Phosphines bearing *para*- and *meta*-electron-donating groups favored the reaction (entries 2, 4, 7, 8, 11, and 12, Table 2). Particularly, the reaction of tris

Table 2
Synthesis of symmetric $[(E)\text{-}R^1R^2R^3PCH{=}CHPR^1R^2R^3][OTf]_2$ from $R^1R^2R^3P$ and $TfOCH_2CF_2H$



Entry	$R^1R^2R^3P$	Ratio[a]	Conditions (°C/h)	Yield[b] (%) **3**[c] or **4**
1	$(p\text{-}MeC_6H_4)_3P$ (**1b**)	1:1	rt/12	6 (**3b**)
2	$(p\text{-}MeC_6H_4)_3P$ (**1b**)	1:1	120/6	70 (**3b**)
3	$(m\text{-}MeC_6H_4)_3P$ (**1c**)	1:1	rt/12	5 (**4c**)
4	$(m\text{-}MeC_6H_4)_3P$ (**1c**)	1:1	120/6	80 (**3c**)
5	$(o\text{-}MeC_6H_4)_3P$ (**1d**)	1:1	120/6	49 (**4d**)[d]
6	$(o\text{-}MeOC_6H_4)_3P$ (**1e**)	1:1	120/6	94 (**4e**)[d]
7	$(p\text{-}MeOC_6H_4)_3P$ (**1f**)	1:1.2	120/6	74 (**3f**)
8	$(m\text{-}MeOC_6H_4)_3P$ (**1g**)	1:1.2	120/6	51 (**3g**)
9	$(p\text{-}ClC_6H_4)_3P$ (**1h**)	1:1	120/24	41 (**3h**)
10	$(p\text{-}FC_6H_4)_3P$ (**1i**)	1:1	120/24	79 (**3i**)
11	(Biphenyl)PPh_2 (**1j**)	1:1	120/24	72 (**3j**)
12	$(p\text{-}MeOC_6H_4)_2PPh$(**1k**)	1:1	120/6	91 (**3k**)
13	Ph_2PCy (**1l**)	1:1	120/15	66 (**4l**)[d]
14	Ph_2PCH_3 (**1m**)	1:1	120/8	72 (**3m**)
15	$PhP(CH_3)_2$ (**1n**)	1:1	rt/72	67 (**4n**)[e]
16	Cy_3P (**1o**)	1:1	rt/12	55 (**4o**)
17	Cy_3P (**1o**)	2:1	120/8	63 (**3o**)
18	$P(n\text{-}Bu)_3$ (**1p**)	2:1	120/6	Complicated

[a] The molar ratio of $R^1R^2R^3P$ and HCF_2CH_2OTf.
[b] Isolated yield.
[c] Trace of fluorides was observed in most cases, which was determined by ^{19}F NMR (see SI).[15] Efforts to remove these byproducts by recrystallization failed. All the products (**3**) were obtained in *E*-configuration.
[d] See Ref. 16.
[e] Crude product. Bis(phosphonium)ethylene was not formed in this reaction, according to NMR spectroscopy.

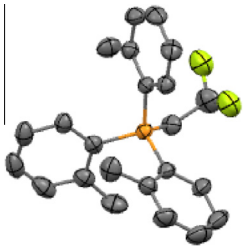


Figure 2. ORTEP diagrams of **4d**. Ellipsoids are shown at the 50% probability level. Hydrogens and anions are omitted for clarity.

(*para*-methylphenyl)phosphine (**1b**) with **2a** afforded **3b** even at room temperature, albeit in a low yield (entry 1, Table 2). However, phosphines with *ortho*-substitution on the phenyl rings frustrated the transformation, which gave only monophosphonium salts (**4d**, **4e**, entries 5 and 6, Table 2).[16] The structure of **4d** was strictly confirmed by X-ray crystallography (Fig. 2).[14] We speculate that the steric hindrance of the *ortho*-substituents on phenyl rings might cause the failure of the conversion.[16]

Using arylalkylphosphines and alkylphosphines instead of arylphosphines as substrates, the reactions with **2a** became complicated (entries 13–18, Table 2). For example, treatment of **1l** with **2a** at 120 °C for 15 h gave monophosphonium salt **4l** in 66% yield (entry 13, Table 1),[16] whereas **1m** reacting with **2a** at 120 °C for 8 h provided bis(phosphonium)ethylene **3m** in 72% yield (entry 14, Table 2). Dimethyl(phenyl)phosphine (**1n**) reacted with **2a** at room temperature for 72 h, after standard workup, affording crude **4n** in a moderate yield (entry 15, Table 2). Heating the reaction mixture to 120 °C, however, gave a chaotic mixture of salts. Interestingly, the reaction of tricyclohexylphosphine (**1o**) with **2a** at room temperature for 12 h furnished **4o** in 55% yield, while the similar mixture reacted at 120 °C for 8 h provided **3o** in 63% yield (entries 16 and 17, Table 2). In the case of P(*n*-Bu)$_3$ (**1p**), no pure bis(phosphonium)ethylene product was obtained under the standard reaction conditions according to NMR spectroscopy analysis (entry 18, Table 2). The elusive electronic and steric effects that arose from the small variations in alkyl groups made the reactions a little difficult to be sought out.

In addition, extensive efforts were directed to the synthesis of asymmetric $[Ph_3PCH{=}CHPR_3]^{2+}\bullet 2X^-$ from $[Ph_3PCH_2CF_2H][OTf]$ and R_3P (R = *p*-MeC_6H_4, *m*-MeC_6H_4, *p*-MeOC_6H_4, Cy). The reactions did occur, but unfortunately, no pure asymmetric vinylenebis(trialkylarylphosphonium) salts were isolated. The possible nucleophilic vinylic substitution of the phosphonium groups of the products by another molecule of R_3P eventually led to mixtures of symmetric and asymmetric bis(phosphonium)ethylenes.[8] HCF_2CH_2I and other difluoroethyl esters (like $TsOCH_2CF_2H$ and $AcOCH_2CF_2H$) were also employed to synthesize bis(phosphonium)-ethylene salts. The negative results (such as the incomplete transformation of the starting materials and the formation of massive unknown byproducts) indicated that **2a** may be the best reagent for this reaction.

Based on the results above, we envisioned a reaction mechanism in Scheme 1, which might involve S_N2-type substitution, nucleophilic addition, and β-F elimination. First, nucleophilic substitution of **2a** by **1** at the α-carbon gives monophosphonium salt **4**. Intermediate **4** is susceptible to β-F elimination providing **5** and **6** in the presence of a second phosphine (or F^-) because of the favorable leaving ability of fluoride.[13,16] Compound **5** would be easily dissociated at high temperature to release **1** and HF. Intermediate **6** is nucleophilically attacked by **1** to form **7**, which undergoes β-F elimination to generate **8**. Reaction of **8** with excess **2a** finally affords bis(phosphonium)ethylene **3**. When R^1, R^2, or R^3 is an alkyl group, the tendency of α-deprotonation of phosphoniums at R^1, R^2, or R^3 site, competing with CH_2CF_2H group, is rationalized, which might illustrate the frustrated transformation of alkylarylphosphines and alkylphosphines. Nonetheless, the whole mechanism of the reaction is still unclear.

In conclusion, we have developed a facile method to the synthesis of vinylenebis(trialkylphosphonium) salts from aryl-, alkyl-, and arylalkylphosphines by using $TfOCH_2CF_2H$ as reagent. The reactions proceeded at 120 °C under solvent-free conditions to afford (*E*)-bis(phosphonium)ethylenes in good to high yields. The reaction temperature and the substituents on the phenyl rings of phosphines greatly influence the reaction. Phosphines bearing *para*- and *meta*-substituents on the phenyl rings favored the formation of bis(phosphonium)ethylenes, whereas the substrates with *ortho*-substitution on phenyl rings gave only monophosphonium salts.[16] The reactions of arylalkylphosphines and alkylphosphines are elusive but some of them can also provide the desired products. Further mechanistic study and the application of these vinylenebis(trialkylarylphosphonium) salts are ongoing in our lab.

Acknowledgements

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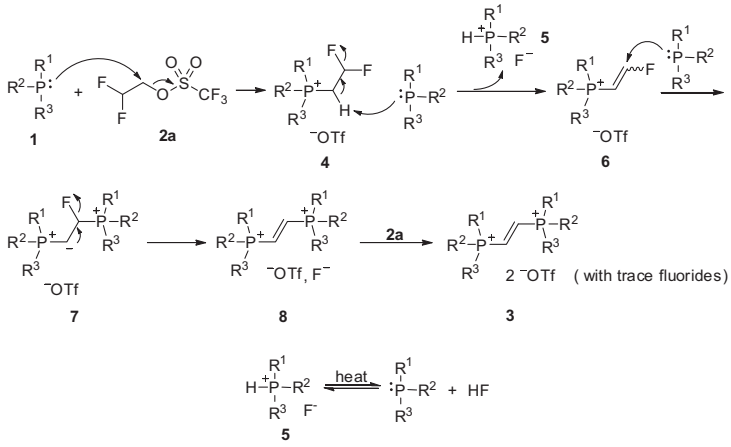

Scheme 1. Proposed mechanism for the solvent-free synthesis of bis(phosphonium)ethylenes from phosphines (**1**) and **2a**.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.09.092.

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16. The addition of KF into the reaction mixture can facilitate the production of vinylenebis(trialkylarylphosphonium) triflate. It was found that the reaction of **1d** (1 equiv) with $TfOCH_2CF_2H$ (**2a**, 1 equiv) at 120 °C for 6 h in the presence of 2 equiv of KF gave **3d** in 48% yield, while treatment of **1e** or **1l** (1 equiv) with **2a** (1 equiv) and KF (2 equiv) at 120 °C for 6 h or 15 h, respectively, afforded a mixture of monophosphonium and vinylenebis(phosphonium) salts. We appreciate the reviewer for the suggest.