

Novel Reaction Course of Alkenes to Phosphonium Salts

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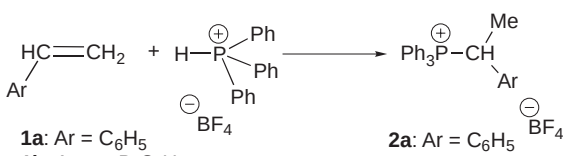
The reaction of styrenes with triphenylphosphine in the presence of acid gave the corresponding 1-arylethylphosphonium salts in 76–82% yields. Indene also reacted with triphenylphosphine and tetrafluoroboric acid to afford 1-indanyltriphenylphosphonium tetrafluoroborate in 72% yield.

From the original work of Wittig and Geissler, Wittig reagents have played an important role in the synthesis of olefins. Many natural-product syntheses utilize this method.[1] These phosphonium salts are generally synthesized by the reaction of alkyl halides with triphenylphosphine, or by the reaction of alcohols with triphenylphosphine in the presence of acids.[2] We have reported the synthesis of 3-hydroxyalkylphosphonium salts by the reaction of methylenetriphenylphosphorane with epoxides, or by the reaction of trimethylene oxide with triphenylphosphine in the presence of acid, which further reacted with aldehydes to give the corresponding homoallylic alcohols in good yields.[3] However, there is no report on the synthesis of phosphonium salts from alkenes. During the course of our studies on the reactivity of the Wittig reaction, we encountered difficulty in the synthesis of 1-arylethyltriphenylphosphonium salts with electron-withdrawing groups at the *para* position.[4] These results prompted us to investigate an alternative synthesis of phosphonium salts by the reaction of olefins with triphenylphosphine. We report herein on a simple synthesis of 1-arylethylphosphonium and related phosphonium salts from alkenes.

Results and Discussion

We first tried the reaction of styrene with triphenylphosphine in the presence of tetrafluoroboric acid. When a mixture of styrene, triphenylphosphine, and tetrafluoroboric acid was heated to 145 °C for 1 h, a colorless solid formed. Recrystallization from ethanol afforded 1-phenylethyltriphenylphosphonium tetrafluoroborate (**2a**) in 82% yield (Scheme 1). When hydrogen bromide was used as an acid, the corresponding phosphonium bromide (**2a′**) was obtained in a similar manner



1a: Ar = C_6H_5
1b: Ar = *p*-BrC_6H_4
1c: Ar = *p*-ClC_6H_4
1d: Ar = *p*-$MeOC_6H_4$
1e: Ar = *p*-MeC_6H_4

2a: Ar = C_6H_5
2b: Ar = *p*-BrC_6H_4
2c: Ar = *p*-ClC_6H_4
2d: Ar = *p*-$MeOC_6H_4$
2e: Ar = *p*-MeC_6H_4

Scheme 1.

Table 1. Reaction of **1** with Triphenylphosphine in the Presence of Acid

Styrene	Acid	Conditions		Product (Yield/%)	
		Temp/°C	Time/min	**2**	
1a	HBF_4	145	60	**2a**	82
1a	HBr	145	50	**2a′**	80
1b	HBF_4	180	40	**2b**	81
1b	HBr	180	40	**2b′**	82
1c	HBF_4	170	30	**2c**	76
1c	HBr	170	50	**2c′**	82
1d	HBF_4	170	50	**2d**	—
1d	HBr	170	50	**2d′**	82
1e	HBF_4	170	30	**2e**	81
1e	HBr	170	40	**2e′**	82

(Table 1). When trifluoroacetic acid was used as an acid, the starting styrene and triphenylphosphonium trifluoroacetate were recovered. Previously, 1-phenylethyltriphenylphosphonium bromide (**2a′**) has been synthesized by the reaction of 1-phenylethyl bromide with triphenylphosphine.[5] However, substituted 1-arylethyl bromides must be synthesized from substituted acetophenones via a two-step reaction. Since many substituted styrenes are commercially available, our method requires only a one-step reaction.

We next tried the reaction of other alkenes with triphenylphosphine to investigate the scope and limitation of this methodology. When allylbenzene (**1f**) was used as an olefin, 1-phenylpropyltriphenylphosphonium tetraphenylborate (**2f**) was obtained in 25% yield (Scheme 2). Since a benzyl cation is more stable than a dialkyl substituted secondary cation, it can be assumed that the initially formed secondary cation easily rearranged to a benzyl cation, which finally gave **2f** (Scheme 3). When stilbene (**1g**) was used as a substrate, only a small amount of phosphonium salt **2g** was obtained. Almost all of the stilbene had sublimed. However, when the reaction was carried out in a microwave oven, 51% of the phosphonium salt **2g** was obtained after recrystallization (Scheme 4). Probably, the sublimation property of **1g** was suppressed by heating in a microwave oven.

Since indene (**1h**) is a cyclic olefin, we next tried the reaction with triphenylphosphine in the presence of acid. The treat-

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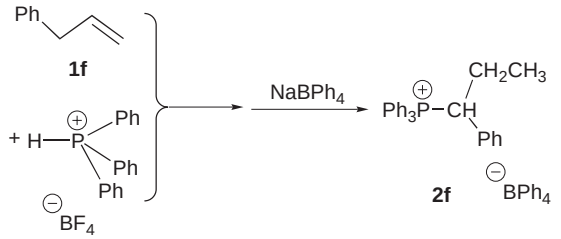
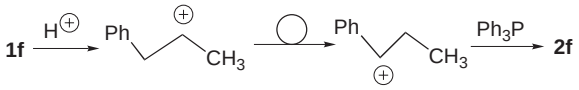
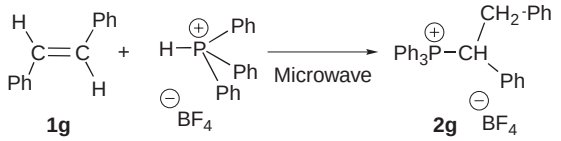


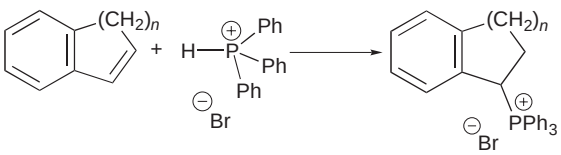
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

ment of **1h** with triphenylphosphonium bromide at 160 °C resulted in the formation of phosphonium salt **2h** in 72% yield. Formerly, Bestmann et al. synthesized 2-indyltriphenylphosphonium bromide **2h** by a two-step reaction of triphenylphosphine with *o*-bromoethylbenzyl bromide, which was synthesized by a further two-step reaction.[6] Thus, this method provides a convenient route to phosphonium salts containing an indanyl moiety. Similarly, 1-tetrahydronaphthyltriphenylphosphonium bromide (**2i**) was obtained in 62% yield (Scheme 5).[7] Recently, vinylphosphonium salts were synthesized by the metal-catalyzed addition of triphenylphosphine with methanesulfonic acid.[8] Although products of the Wittig reaction are alkenes, these products themselves can be used in this alternative and convenient route to generate a variety of other phosphonium salts. In conclusion, we have developed a general synthesis of α-substituted benzyl-type phosphonium salts from the corresponding alkenes.

Experimental

General. All solvents were distilled before use, and no further treatment was carried out. NMR spectra were measured on a Varian Innova-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C). The melting points were not corrected. The reagents were purchased from TCI and used without purification.

Reaction of Styrenes with Triphenylphosphonium Fluoroborate. A mixture of triphenylphosphine (0.79 g, 3.0 mmol) and aq HBF_4 (48%, 0.49 g, 2.7 mmol) was heated at 120 °C for 30 min, and then styrene (0.28 g, 2.7 mmol) was added. The reaction mixture was heated to 145 °C for 1 h and cooled to rt. The obtained colorless solid was recrystallized from ethanol to give colorless crystals of phosphonium salt **2a** (0.90 g, 2.2 mmol). mp 192–194 °C. ^{1}H NMR ($CDCl_3$) δ 1.85 (dd, 3H, $J = 7.2$ Hz, $J_{HP} = 18.8$ Hz, CH_3), 5.27 (dq, 1H, $J = 7.2$ Hz, $J_{HP} = 14.4$ Hz, CH), 6.90–7.35 (m, 5H, Ph), 7.50–7.82 (m, 15H, PPh_3). ^{13}C NMR ($CDCl_3$) δ 17.35 (d, $J_{PC} = 2$ Hz, CH_3), 36.22 (d, $J_{PC} = 44$ Hz), 117.27 (d, $J_{PC} = 83$ Hz), 129.28, 130.26, 130.48, 130.60, 133.26, 134.57, 135.41 (Ph). Anal. Found: C, 68.75; H, 5.33%. Calcd for $C_{24}H_{24}BF_4P$: C, 68.85; H, 5.41%. **2b**: Colorless crystals, mp 149–151 °C. ^{1}H NMR ($CDCl_3$) δ 1.80 (dd, 3H, $J = 7.2$ Hz, $J_{HP} = 18.8$ Hz, CH_3), 5.46 (dq, 1H, $J = 7.2$ Hz, $J_{HP} = 14.4$ Hz, CH), 6.87 (dd, 2H, $J_{HP} = 2.4$ Hz, $J = 8.8$ Hz, 2H, Ar), 7.32 (d, 2H, $J = 8.8$ Hz, Ar), 7.61–7.83 (m, 15H, PPh_3). ^{13}C NMR ($CDCl_3$) δ 17.20 (CH_3), 35.05 (d, $J_{PC} = 44$ Hz, CH), 117.22 (d, $J_{PC} = 82$ Hz, *ipso*-PPh_3), 123.53, 130.62, 132.06, 132.35, 133.96, 134.55, 135.43 (Ar). Anal. Found: C, 58.57; H, 4.35%. Calcd for $C_{26}H_{23}BBrF_4P$: C, 58.70; H, 4.47%. **2c**: Colorless crystals, mp 192–194 °C. ^{1}H NMR ($CDCl_3$) δ 1.80 (dd, 3H, $J = 7.2$ Hz, $J_{HP} = 18.8$ Hz, CH_3), 5.40 (dq, 1H, $J = 7.2$ Hz, $J_{HP} = 14.4$ Hz, CH), 6.93 (dd, 2H, $J_{HP} = 2.4$ Hz, $J = 8.8$ Hz, Ar), 7.16 (d, 2H, $J = 8.8$ Hz, Ar), 7.60–7.83 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$) δ 17.26 (CH_3), 35.04 (d, $J_{PC} = 44$ Hz, CH), 117.26 (d, $J_{PC} = 82$ Hz, *ipso*-PPh_3), 129.39, 130.60, 131.87, 132.00, 134.00, 134.55, 135.39 (Ar). Anal. Found: C, 63.90; H, 4.74%. Calcd for $C_{26}H_{23}BClF_4P$: C, 63.93; H, 4.85%. **2d**: Colorless crystals, mp 173–174 °C. ^{1}H NMR ($CDCl_3$) δ 1.81 (dd, 3H, $J = 7.6$ Hz, $J_{HP} = 19.2$ Hz, CH_3), 3.76 (s, 3H, OMe), 5.33 (dq, 1H, $J = 7.6$ Hz, $J_{HP} = 15.2$ Hz, CH), 6.72 (d, 2H, $J = 8.4$ Hz, Ar), 6.88 (dd, 2H, $J_{HP} = 2.0$ Hz, $J = 8.4$ Hz, Ar), 7.57–7.82 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$) δ 17.41 (CH_3), 35.31 (d, $J_{PC} = 44$ Hz, CH), 55.58 (OMe), 114.60 (d, $J_{PC} = 2$ Hz, *ipso*-C_6H_4OMe), 117.50 (d, $J_{PC} = 82$ Hz, *ipso*-PPh_3), 124.62 (d, $J_{PC} = 5$ Hz, *m*-C_6H_4OMe), 130.48 (d, $J_{PC} = 12$ Hz, *m*-PPh_3), 131.49 (d, $J_{PC} = 6$ Hz, *o*-C_6H_4OMe), 134.58 (d, $J_{PC} = 9$ Hz, *o*-PPh_3), 135.32 (d, $J_{PC} = 3$ Hz, *p*-PPh_3), 160.25 (d, $J_{PC} = 3$ Hz, *p*-MeO). Anal. Found: C, 67.29; H, 5.42%. Calcd for $C_{27}H_{26}BF_4OP$: C, 66.96; H, 5.41%. **2e**: Colorless crystals, mp 173–174 °C. ^{1}H NMR ($CDCl_3$) δ 1.82 (dd, 3H, $J = 7.2$ Hz, $J_{HP} = 19.2$ Hz, CH_3), 2.29 (s, 3H, CH_3), 5.23 (dq, 1H, $J = 7.2$ Hz, $J_{HP} = 14.4$ Hz, CH), 6.81 (dd, 2H, $J_{HP} = 2.0$ Hz, $J = 8.0$ Hz, Ar), 6.99 (d, 2H, $J = 8.0$ Hz, Ar), 7.55–7.78 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$) δ 17.44 (CH_3), 21.37 ($TolCH_3$), 35.82 (d, $J_{PC} = 44$ Hz, CH), 117.50 (d, $J_{PC} = 82$ Hz, *ipso*-PPh_3), 129.65, 130.35, 130.36, 130.51, 134.86, 135.01, 138.93. Anal. Found: C, 69.25; H, 5.60%. Calcd for $C_{27}H_{26}BF_4P$: C, 68.93; H, 5.62%.

Similarly, phosphonium bromides were synthesized in the same scale. **2a′**: Colorless crystals, mp 230–232 °C (lit.[9] mp 224–225 °C). **2b′**: Colorless crystals, mp 233–235 °C. ^{1}H NMR ($CDCl_3$) δ 1.77 (dd, 3H, $J = 6.8$ Hz, $J_{HP} = 18.8$ Hz, CH_3), 6.97 (dq, 1H, $J = 6.8$ Hz, $J_{HP} = 13.6$ Hz, CH), 7.09 (dd, 2H, $J_{HP} = 2.4$ Hz, $J = 8.8$ Hz, Ar), 7.27 (d, 2H, $J = 8.8$ Hz, Ar), 7.56–7.86 (m, 15H, PPh_3). ^{13}C NMR ($CDCl_3$) δ 17.08 (CH_3), 33.98 (d, $J_{PC} = 43$ Hz, CH), 117.69 (d, $J_{PC} = 82$ Hz, *ipso*-PPh_3), 123.17, 130.48, 132.02, 132.64, 132.91, 134.79, 135.14 (Ar). Anal. Found: C, 59.34; H, 4.41%. Calcd for $C_{26}H_{23}Br_2P$: C, 59.05; H, 4.45%. **2c′**: Colorless crystals, mp 230–232 °C. ^{1}H NMR ($CDCl_3$) δ 1.79 (dd, 3H, $J = 7.2$ Hz, $J_{HP} = 19.2$ Hz, CH_3), 7.08–7.21 (m, 5H, CH and Ar), 7.62–7.94 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$) δ 17.15 (CH_3), 34.06 (d, $J_{PC} = 43$ Hz, CH), 117.60 (d, $J_{PC} = 82$ Hz, *ipso*-PPh_3), 129.07, 130.48, 132.17, 132.33, 134.75, 134.90,

135.00 (Ar). Anal. Found: C, 64.82; H, 4.81%. Calcd for $C_{26}H_{23}BrClP$: C, 64.49; H, 4.84%. **2e′**: Colorless crystals, mp 253–254 °C. ^{1}H NMR ($CDCl_3$) δ 1.79 (dd, 3H, $J = 6.8$ Hz, $J_{HP} = 19.6$ Hz, CH_3), 2.21 (s, 3H, CH_3), 6.67 (dq, 1H, $J = 6.8$ Hz, $J_{HP} = 13.6$ Hz, CH), 6.95 (d, 2H, $J = 8.0$ Hz, Ar), 7.03 (d, 2H, $J = 8.0$ Hz, Ar), 7.55–7.86 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$) δ 17.38 (CH_3), 21.38 (TolCH_3), 34.80 (d, $J_{PC} = 42$ Hz, CH), 117.99 (d, $J_{PC} = 82$ Hz, *ipso*-PPh_3), 129.65, 130.32, 130.43, 134.86, 135.01, 138.93. Anal. Found: C, 70.29; H, 5.68%. Calcd for $C_{27}H_{26}BrP$: C, 70.18; H, 5.64%.

Reaction of Allylbenzene with Triphenylphosphonium Fluoroborate. After a mixture of triphenylphosphine (0.52 g, 2.0 mmol) and aq HBr (48%, 0.30 g, 1.8 mmol) was heated at 110 °C for 30 min, then allylbenzene (0.21 g, 1.8 mmol) was added. The reaction mixture was heated at 160 °C for 1 h and cooled to rt. The resulting mixture was dissolved into acetone (10 mL) and added to a solution of sodium tetraphenylborate (0.34 g, 1.0 mmol) in acetone (10 mL). Colorless crystals of triphenylphosphonium tetraphenylborate immediately precipitated, which were filtered and the filtrate was evaporated to give a pale-brown solid. Methanol (10 mL) was added to this solid to afford colorless crystals, which were recrystallized from acetone to afford colorless crystals of (1-phenylpropyl)triphenylphosphonium tetraphenylborate (0.26 g, 0.36 mmol). **2f**: Colorless crystals, mp 207–208 °C. ^{1}H NMR (CD_3SOCD_3) δ 0.83 (t, 3H, $J = 6.8$ Hz, Me), 1.90–2.05 (m, 1H, C<u>H</u>H), 2.18–2.27 (m, 1H, CH<u>H</u>), 5.27 (brt, 1H, $J = 13.0$ Hz, CH), 6.70–7.20 (m, 22H, *o*-Ph + BPh_4), 7.25–7.40 (m, 3H, Ph), 7.53–7.90 (PPh_3). Anal. Found: C, 87.29; H, 6.75%. Calcd for $C_{51}H_{46}BP$: C, 87.42; H, 6.62%.

Reaction of Stilbene 1g with Triphenylphosphonium Fluoroborate. A mixture of triphenylphosphine (0.52 g, 2.0 mmol), aq HBF_4 (48%, 0.44 mL, 2.0 mmol), and **1g** (0.49 g, 2.0 mmol) was heated in microwave oven (600 W) for 3 min. The obtained colorless solid was recrystallized from ethanol to give colorless crystals of (1,2-diphenylethyl)triphenylphosphonium tetrafluoroborate (0.56 g, 1.05 mmol). **1g**: Colorless crystals. mp 211–213 °C. ^{1}H NMR ($CDCl_3$) δ 3.26 (dt, 1H, $J = 5.2$, 8.0 Hz, PhC<u>H</u>H), 3.64 (brdd, 1H, $J = 8.0$, 12.4 Hz, PhC<u>H</u>H), 5.11 (brt, 1H, $J = 8.0$ Hz, CH), 6.80–7.30 (m, 10H, Ph), 7.57–7.87 (m, 15H, PPh_3). ^{13}C NMR ($CDCl_3$) δ 37.16 (CH_2), 44.41 (d, $J_{PC} = 43$ Hz, CH), 117.00 (d, $J_{PC} = 82$ Hz, *ipso*-PPh_3), 127.37, 128.90, 129.07, 129.38, 129.60, 130.58, 130.79, 130.96, 134.64, 135.73, 135.87. Anal. Found: C, 72.47; H, 5.32%. Calcd for $C_{32}H_{28}BF_4P$: C, 72.22; H, 5.34%.

Reaction of Indene 1h with Triphenylphosphonium Bromide. A mixture of triphenylphosphine (0.79 g, 3.0 mmol) and aq HBr (48%, 0.45 g, 2.7 mmol) was heated to 110 °C for 30 min, and then indene **1h** (0.31 g, 2.7 mmol) was added. The reaction mixture was heated to 160 °C for 1 h and cooled to rt. The obtained colorless solid was recrystallized from ethanol to give colorless crystals of 1-indanyltriphenylphosphonium bromide (0.75 g, 1.94 mmol). **2h**: Colorless crystals, mp 221–222 °C (lit.[6] mp 220–222 °C). ^{1}H NMR ($CDCl_3$) δ 1.62 (m, 1H, C<u>H</u>H), 2.35 (m, 1H, C<u>H</u>H), 2.71 (m, 1H, C<u>H</u>H), 3.28 (m, 1H, C<u>H</u>H), 6.80 (m, 1H, Ar), 6.92–7.05 (m, 2H, Ar), 7.19 (m, 1H, Ar), 7.24 (m, 1H, P-CH), 7.62 (m, 6H, Ph), 7.73 (m, 3H, Ph), 7.86 (m, 6H, Ph). ^{13}C NMR ($CDCl_3$) δ 27.23 (CH_2), 31.12 (CH_2), 39.47 (d, $J_{PC} = 43$ Hz, CH), 118.43 (d, $J_{PC} = 83$ Hz, *ipso*-PPh_3), 125.32, 126.86, 127.18, 129.24, 130.40, 134.23, 134.44, 134.90, 146.32.

Similarly, 1,2,3,4-tetrahydro-1-naphthyltriphenylphosphonium bromide (**2i**) was obtained in 69% yield. **2i**: Colorless crystals, mp 256–258 °C. ^{1}H NMR ($CDCl_3$) δ 1.29–1.38 (m, 1H, C<u>H</u>H), 1.48–1.64 (m, 2H, CH_2), 1.95–2.12 (m, 1H, CH_2), 2.38 (brd, 1H, $J = 15.6$ Hz, C<u>H</u>H), 2.87–3.02 (m, 1H, C<u>H</u>H), 6.81–7.14 (m, 5H, Ar + CH), 7.57–7.92 (PPh_3). ^{13}C NMR ($CDCl_3$) δ 21.35 (d, $J_{PC} = 5$ Hz, CH_2), 24.73, 29.08, 34.49 (d, $J_{PC} = 42$ Hz, CH_2), 118.68 (d, $J_{PC} = 82$ Hz, *ipso*-PPh_3), 126.40 (d, $J_{PC} = 4$ Hz, Ar), 126.99 (d, $J_{PC} = 7$ Hz, Ar), 128.25 (d, $J_{PC} = 4$ Hz, Ar), 129.58 (d, $J_{PC} = 4$ Hz, Ar), 130.33 (d, $J_{PC} = 12$ Hz, PPh_3), 131.21 (d, $J_{PC} = 5$ Hz, Ar), 134.68 (d, $J_{PC} = 9$ Hz, PPh_3), 134.75 (PPh_3), 141.82 (d, $J_{PC} = 5$ Hz, Ar). Elemental analysis was carried out on its tetrafluoroborate. mp 235–236 °C. Anal. Found: C, 69.89; H, 5.58%. Calcd for $C_{28}H_{26}BF_4P$: C, 70.02; H, 5.46%.

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