

Unusual Reaction Course of Styrenes to 2-Arylethyltriphenylphosphonium Salts

Kentaro Okuma,* Koichiro Yoshitake, Toshiharu Izaki, Keiko Yoshida, and Kosei Shioji

Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-0180

Received February 13, 2007; E-mail: kokuma@fukuoka-u.ac.jp

1-Arylethyltriphenylphosphonium bromides thermally rearranged to 2-arylethyltriphenylphosphonium bromides. Direct formation of 2-arylethylphosphonium bromides was achieved by reacting styrene, HBr, and triphenylphosphine. On the other hand, thermolysis of 1-indanyltriphenylphosphonium bromide gave indene and triphenylphosphonium bromide. From deuterium and ^{13}C-labeled experiments, the interconversion of primary and secondary cation intermediates was suggested. No neighboring phenyl group (phenonium cation intermediate) interaction was observed.

From the original work of Wittig and Geissler, Wittig reagents have played an important role in the synthesis of olefins.[1] Substituted 2-arylethyltriphenylphosphonium salts **1** are very important precursors for the synthesis of benzo[*j*]fluoranthene,[2] (*Z*)-penta-1,3-dienes,[3] quinuclidines, which are antiarrhythmic agents,[4] and aryl-substituted alkenes.[5] Methods for the preparation of phenethyltriphenylphosphonium salts **1** include the reaction of phenethyl halides with triphenylphosphine,[6] the reaction of 2-phenylethanol with triphenylphosphine and acids,[7] and the reaction of methylenetriphenylphosphorane with substituted benzyl halides.[3] However, these methods are limited due to the availability of substituted 2-arylethyl halides and 2-arylethanols. We have reported a novel synthesis of substituted 1-arylethyltriphenylphosphonium salts **2** by the reaction of styrenes **3** with triphenylphosphine in the presence of acid.[8] Recent reports on the palladium-catalyzed synthesis of alkylphosphonium salts[9] and deuterium-labeled synthesis of primary phosphonium salts[10] prompted us to investigate the thermal transformation of **2** to **1**. We report herein a new synthesis of **1** from 1-arylethylphosphonium salts **2** and one-pot synthesis of salts **1** from substituted styrenes **3**.

Results and Discussion

Generally, secondary carbocations are more stable than primary carbocations, whereas, at higher temperature, steric hindrance is more important for the stability of carbocations. Thus, it should be possible to synthesize primary phosphonium salts by rearrangement of secondary phosphonium salts. We first tried DFT calculations on 1-phenylethyltriphenylphosphonium bromide (**2a**) and phenylethyltriphenylphosphonium bromide (**1a**). As **1a** is an isomer of **2a**, the stabilities of **1a** and **2a** were compared. By means of geometry optimization and frequency calculation at the B3LYP/6-31G(d,p) level,[11] **1a** was calculated to be 21.9 kJ mol^{-1} more stable than **2a** in the ground state (S_0) (Fig. 1). Thus, at elevated temperatures, it is possible that 1-arylethylphosphonium salts **2** will rearrange to 2-arylethylphosphonium salts **1**.

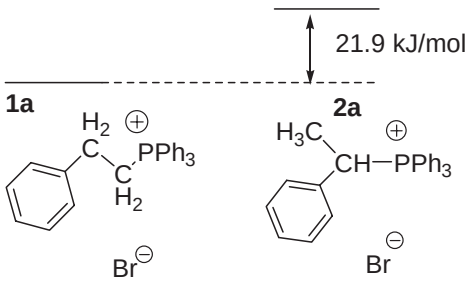
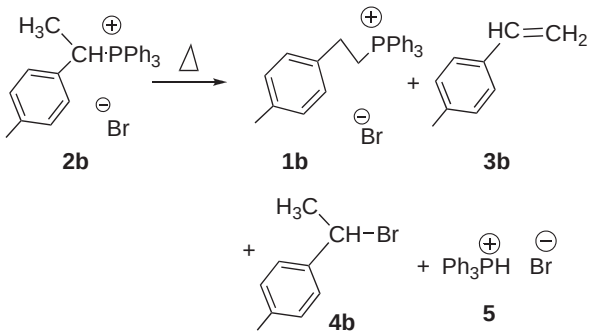


Fig. 1.



Scheme 1.

First, we tried the thermal rearrangement of 1-*p*-tolylethyltriphenylphosphonium bromide (**2b**) under several conditions in an NMR tube (0.05 mmol scale) (Scheme 1). The yields of the products was calculated by integral ratio (NMR) of the products, and they are shown in Table 1. Thermolysis of **2b** under several temperature (220–300 °C) led to **1b** in low yields (Entries 1–6). Only 25% of 2-*p*-tolylethyltriphenylphosphonium bromide (**1b**) formed (Entry 5). However, when salt **2b** was heated at 230–270 °C in the presence of triphenylphosphine (0.1 molar amount), as much as 52% of **2b** was converted into **1b** along with 1-*p*-tolylethyl bromide (**4b**) and *p*-methylstyrene (**3b**) (Entries 7–9). When the reaction was carried out in the presence of 0.3 molar amount of triphenylphosphine, the conversion of **1b** was up to 75% (Entry 11). Further addition of triphenylphosphine did not change the yield of **1b** (Entry 12). Thus, on a preparative scale, the rearrangement was carried out at 260–270 °C in the presence of 0.3 molar amount of triphenylphosphine (Scheme 2). The corresponding

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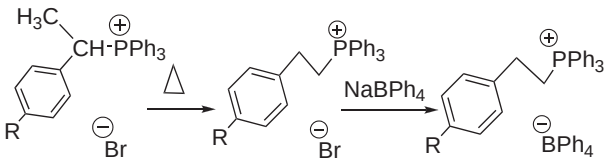
Table 1. Thermal Rearrangement of **2b** to **1b**

	Conditions			Products (Yield/%)			
Entry	Temp/°C	Time/min	Ph_3P/mol amt.	**2b**	**1b**	**4b**	**3b**
1	220	35	0	95	0	0	0
2	230	25	0	75	5	5	0
3	240	25	0	50	5	15	5
4	240	15	0	45	12	15	10
5	260	25	0	45	25	15	15
6	300	15	0	7	10	3	42
7	230	25	0.1	25	15	5	0
8	250	30	0.1	21	52	12	3
9	270	15	0.1	26	43	10	5
10	270	30	0.3	8	72	5	5
11	270	60	0.3	3	75	5	6
12	270	60	0.5	4	76	4	5

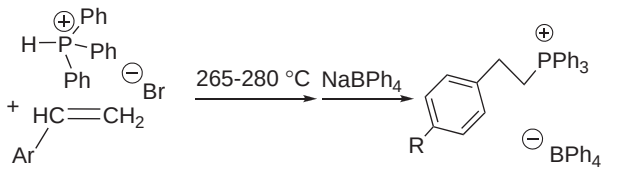


2a, R = H
2b, R = CH_3
2c, R = Cl
2d, R = Br
2e, R = CF_3

1a, R = H
1b, R = CH_3
1c, R = Cl
1d, R = Br
1e, R = CF_3

7a, R = H
7b, R = CH_3
7c, R = Cl
7d, R = Br
7e, R = CF_3

Scheme 2.



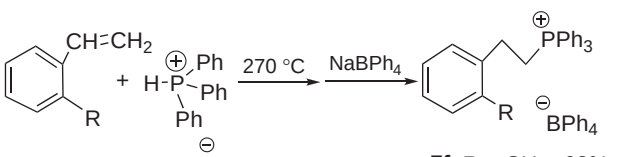
3a: Ar = C_6H_5
3b: Ar = *p*-MeC_6H_4
3c: Ar = *p*-ClC_6H_4
3d: Ar = *p*-BrC_6H_4
3e: Ar = *p*-$CF_3C_6H_4$

7a: Ar = C_6H_5
7b: Ar = *p*-MeC_6H_4
7c: Ar = *p*-ClC_6H_4
7d: Ar = *p*-BrC_6H_4
7e: Ar = *p*-$CF_3C_6H_4$

Scheme 3.

Table 2. Thermal Rearrangement of **2**

Salt **2**	Temp/°C	Time/min	**7**	Yield/%
2a	270	50	**7a**	60
2b	270	50	**7b**	61
2c	265	45	**7c**	62
2d	260	45	**7d**	62
2e	270	40	**7e**	61



3f, R = CH_3
3g, R = Cl
5

7f, R = CH_3 62%
7g, R = Cl 61%

Scheme 4.

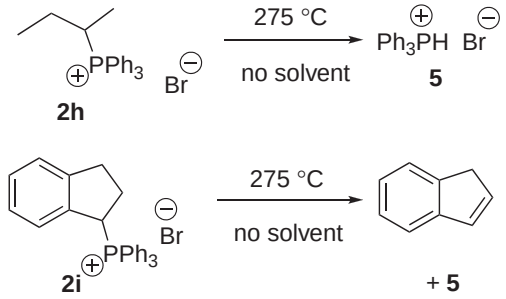
2-arylethylphosphonium bromides (**1a**–**1e**) were obtained in moderate yields. Since **1a**–**1e** are hygroscopic glassy solids, elemental analyses were carried out by changing them into their tetraphenylborates (**7a**–**7e**). The result are shown in Table 2.

Since 1-arylethyltriphenylphosphonium bromides **2** were synthesized by the reaction of styrenes **3** with triphenylphosphonium bromide,[8] an one-pot synthesis of 2-arylethyltriphenylphosphonium bromides **1** from styrenes **3** was carried out. As shown in Scheme 3, 2-(*p*-chlorophenyl)ethyltriphenylphosphonium bromide (**1c**) (then **7c**) was readily obtained from *p*-chlorostyrene (**3c**) by treatment with triphenylphosphine hydrobromide. This transformation constitutes an extremely practical one-pot synthesis of 2-arylethyltriphenylphosphonium salts. Unreacted styrene and by-products, such as hydrogen bromide and 1-*p*-chlorophenyl-1-bromoethane, were easily separated by treating with a base and washing with ether. It should be noted that this salt has previously been synthesized from *p*-chlorostyrene by a multi-step procedure.[12]

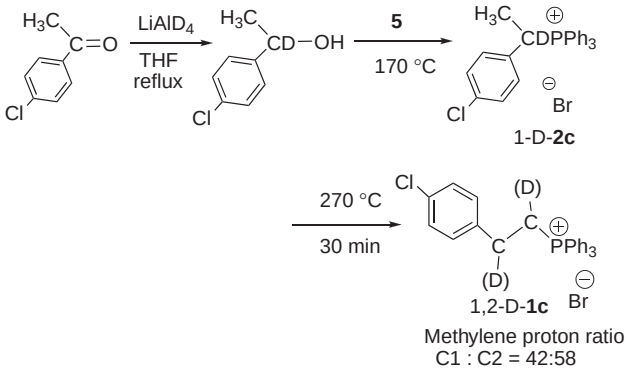
Other *o*-substituted styrenes (**3f** and **3g**) also rearranged to 2-arylethyltriphenylphosphonium bromides (**1f** and **1g**) in moderate yields (Scheme 4).

We next tried the reaction of other primary phosphonium salts. Heating of *sec*-butyltriphenylphosphonium bromide (**2h**) at 275 °C for 20 min led to triphenylphosphonium bromide. Heating of 1-indanyltriphenylphosphonium bromide (**2i**) at 275 °C for 20 min led to indene and triphenylphosphonium bromide. These results are similar to that of Bestmann et al.[13] They have reported the thermolysis of **2i** under reduced pressure at 300 °C, which results in the formation of indene and triphenylphosphonium bromide (Scheme 5), suggesting that aromatic groups in **2a**–**2g** play an important role in the formation of phosphonium salts **1a**–**1g**.

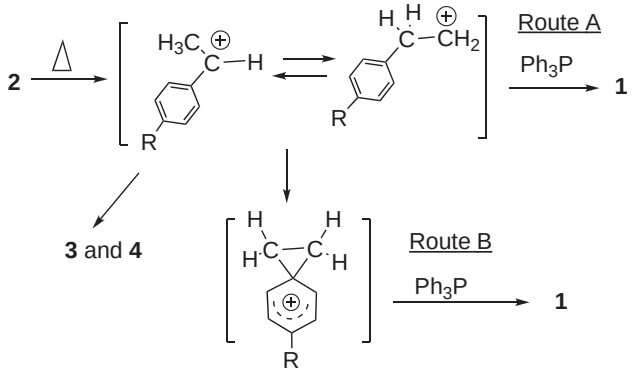
Thus, there are two reaction pathways for the present reaction. Heating of phosphonium salt **2** gives a secondary carbocation. If hydrogen abstraction occurs, styrene **3** is afforded, other hand, if the carbocation reacts with a bromide anion, 1-aryl-1-bromoethane **4** is produced. Quite a few secondary carbocation rearranged to give primary carbocation, which was attacked by triphenylphosphine to give **1** (Route A). In



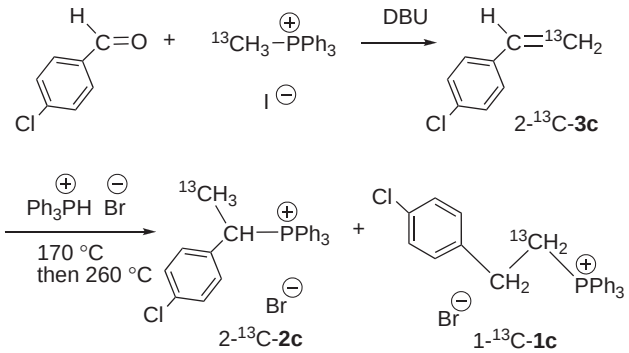
Scheme 5.



Scheme 7.



Scheme 6.



Scheme 8.

the second route, interconversion of the primary and secondary carbocation is stabilized by a neighboring aromatic group (anchimeric assistance).[14,15] The intermediate cation (phenonium ion) is attacked by triphenylphosphine to produce 1-arylethylphosphonium bromide **1** (Route B) (Scheme 6).

To confirm the reaction mechanism, the following deuterium-labeled experiment was carried out (Scheme 7). 1-(*p*-Chlorophenyl)-1-deuteroethyltriphenylphosphonium bromide (1-D-**2c**) was synthesized by the reaction of **5** with 1-(*p*-chlorophenyl)-1-deuteroethanol, prepared from *p*-chloroacetophenone and lithium aluminum-d_4-hydride. Thermolysis of 1-D-**2c** in the presence of triphenylphosphine (0.3 molar amount) gave a mixture of 2-*p*-chlorophenyl-1-deuterioethyltriphenylphosphonium bromide (1-D-**1c**) and 2-(*p*-chlorophenylethyl)-1,2-d_2-triphenylphosphonium bromide (1,2-D-**1c**) (42:58 ratio), suggesting that the rearrangement proceeds through interconversion of primary and secondary carbocation.

Since this result cannot confirm the existence of phenonium cation, we then carried out the ^{13}C-labeled experiment as follows. Treatment of (*p*-chlorophenyl)ethene-2-^{13}C (2-^{13}C-**3c**), prepared from methyl-^{13}C-triphenylphosphonium iodide, DBU, and *p*-chlorobenzaldehyde, with triphenylphosphonium bromide in the presence of triphenylphosphine (0.3 molar amount) resulted in the formation of a mixture of 1-(*p*-chlorophenyl)-2-^{13}C-ethyltriphenylphosphonium bromide (2-^{13}C-**2c**) and 2-(*p*-chlorophenyl)ethyl-1-^{13}C-triphenylphosphonium bromide (1-^{13}C-**1c**) (1:4 ratio) (Scheme 8). This result clearly shows that the reaction does not proceed through phenonium ion intermediates (Route B) but through interconversion of secondary and primary cation intermediates (Route A).

In conclusion, we developed a general synthesis of 2-arylethyltriphenylphosphonium bromides from the corresponding 1-arylethylphosphonium bromides, styrenes, or 1-arylethanols. The reaction might proceed through interconversion of secondary to primary cation intermediates.

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 uncorrected. The reagents were purchased from TCI and used without purification.

Material. 1-Arylethyltriphenylphosphonium bromides **2a**–**2d** were synthesized by the reaction of styrenes with triphenylphosphonium bromide.[8] 2-Arylethyltriphenylphosphonium bromides (**1a**–**1d**) were already reported in the literature.[5,16,17] However, there are no spectroscopic and melting points' data due to their hygroscopic nature.

Synthesis of 1-(*p*-Trifluoromethylphenyl)ethyltriphenylphosphonium Bromide 2e. A mixture of *p*-trifluoromethylstyrene (0.947 g, 5.5 mmol) and triphenylphosphonium bromide prepared from triphenylphosphine (1.31 g, 5.0 mmol) and hydrobromic acid (48% aqueous solution, 0.57 mL, 5.0 mmol) was heated at 170 °C for 20 min and then cooled to rt. The resulting solid was recrystallized from ethanol to give salt **2e** (1.96 g, 3.8 mmol). colorless crystals; mp 226–228 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82 (dd, 3H, $J = 7.6$ Hz, $J_{PH} = 18.8$ Hz, CH_3), 7.29 (dq, 1H, $J = 6.8$ Hz, $J_{PH} = 13.6$ Hz, CH), 7.43 (s, 4H, Ar), 7.62–7.71 (m, 6H, Ph), 7.70–7.83 (m, 3H, Ph), 7.87–7.96 (m, 6H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.11 (CH_3), 34.20 (d, $J_{PC} = 44$ Hz, CH), 117.52 ($J_{PC} = 83$ Hz, PPh_3), 123.86 (q, $J_{CF} = 270$ Hz, CF_3),

125.66 (Ar), 130.40 (Ar), 130.55 (d, $J_{PC} = 12$ Hz, PPh_3), 131.15 (Ar), 134.75 (d, $J_{PC} = 9$ Hz, PPh_3), 135.25 (d, $J_{PC} = 12$ Hz, PPh_3), 138.30 (d, $J_{pc} = 13$ Hz, Ar). Anal. Calcd for $C_{27}H_{23}BrF_3P$: C, 62.93; H, 4.50%. Found: C, 62.72; H, 4.64%.

Thermal Rearrangement of 1-Phenethyltriphenylphosphonium Bromide (2a) to Phenylethyltriphenylphosphonium Bromide (1a). A mixture of phosphonium bromide **2a** (0.67 g, 1.5 mmol) and triphenylphosphine (0.12 g, 0.45 mmol) was heated to 270 °C for 50 min and cooled to rt. The obtained pale brown glassy solid was dissolved in dichloromethane (30 mL), washed with aq. sodium carbonate (5%, 10 mL × 3), dried over magnesium sulfate, and filtered, and the solvent was evaporated to give a mixture of **1a**, triphenylphosphine, and small amount of triphenylphosphine oxide. The glassy solid was crushed, washed with ether (10 mL × 3) to give pale brown glassy solid of **1a**. The solid was dissolved in acetone and was added to a solution of sodium tetraphenylborate (0.41 g, 1.2 mmol) in acetone (10 mL). The suspension was filtered and evaporated to give colorless solid, which was recrystallized from dichloromethane–ether to afford colorless crystals of **7a** (0.61 g, 0.92 mmol). Salt **1a**: hygroscopic glassy solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.03–3.13 (m, 2H, CH_2), 4.20–4.29 (m, 2H, CH_2), 7.36–7.56 (m, 4H, Ar), 7.60–7.95 (m, 15H, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.89 (d, $J_{PC} = 47$ Hz, CH_2), 28.58 (CH_2), 118.37 (d, $J_{PC} = 86$ Hz, PPh_3), 127.28 (Ph), 129.08 (Ph), 130.72 (d, $J_{PC} = 13$ Hz, PPh_3), 133.28 (Ph), 134.01 (d, $J_{PC} = 10$ Hz, PPh_3), 135.81 (PPh_3), 138.41 (d, $J_{PC} = 13$ Hz, Ph). Salt **7a**: colorless crystals. mp 196–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.68–2.80 (m, 4H, CH_2CH_2), 6.76–6.82 (m, 4H, BPh_4), 6.88–6.93 (m, 8H, BPh_4), 7.20–7.26 (m, 13H, Ph and BPh_4), 7.39 (br, 6H, PPh_3), 7.46–7.54 (m, 6H, PPh_3), 7.69–7.76 (m, 3H, PPh_3). ^{13}C NMR (100 MHz, CD_3SOCD_3): δ 22.12 (d, $J_{PC} = 48$ Hz, CH_2), 28.11 (CH_2), 118.86 (d, $J_{PC} = 86$ Hz, PPh_3), 122.22 (BPh_4), 125.95 (BPh_4), 127.50 (Ph), 128.93 (Ph), 129.22 (Ph), 130.92 (d, $J_{PC} = 12$ Hz, PPh_3), 134.27 (d, $J_{PC} = 10$ Hz, PPh_3), 135.64 (PPh_3), 136.18 (BPh_4), 139.53 (d, $J_{PC} = 17$ Hz, Ph), 163.99 (q, $J_{BC} = 49$ Hz, BPh_4). Anal. Calcd for $C_{50}H_{44}BP$: C, 87.46; H, 6.46%. Found: C, 87.08; H, 6.64%. Other reaction was carried out in a similar manner.

Salt **1b**: hygroscopic glassy solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H, TolMe), 2.96–3.07 (m, CH_2), 4.09–4.19 (m, CH_2), 7.03 (d, 2H, $J = 8.0$ Hz, Tol), 7.15 (d, 2H, $J = 8.0$ Hz, Tol), 7.60–7.89 (m, 15H, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.22 (Me), 25.02 (d, $J_{PC} = 48$ Hz, CH_2), 28.15 (CH_2), 117.26 (d, $J_{PC} = 85$ Hz, PPh_3), 128.78 (Tol), 129.74 (Tol), 130.75 (d, $J_{PC} = 12$ Hz, PPh_3), 133.92 (d, $J_{PC} = 10$ Hz, PPh_3), 134.90 (Tol), 135.31 (d, $J_{PC} = 32$ Hz, PPh_3), 136.93 (Tol). Salt **7b**: mp 176–178 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H, CH_3), 2.65–2.78 (m, 4H, CH_2), 6.75–6.83 (m, 6H, Tol + BPh_4), 6.90–6.96 (m, 8H, BPh_4), 7.01 (d, 2H, $J = 8.0$ Hz, Tol), 7.20–7.28 (m, 8H, BPh_4), 7.39 (br, 6H, PPh_3), 7.49–7.58 (m, 6H, PPh_3), 7.70–7.78 (m, 3H, PPh_3). ^{13}C NMR (100 MHz, CD_3SOCD_3): δ 21.22 (Me), 22.53 (d, $J_{PC} = 51$ Hz, CH_2), 27.70 (CH_2), 118.82 (d, $J_{PC} = 86$ Hz, PPh_3), 122.20 (BPh_4), 125.96 (BPh_4), 128.78 (Tol), 129.72 (Tol), 130.88 (d, $J_{PC} = 12$ Hz, PPh_3), 134.20 (d, $J_{PC} = 10$ Hz, PPh_3), 134.82 (Tol), 135.57 (PPh_3), 136.15 (BPh_4), 136.49 (d, $J_{PC} = 21$ Hz, Tol), 163.97 (q, $J_{BC} = 49$ Hz, BPh_4). Anal. Calcd for $C_{51}H_{46}BP$: C, 87.42; H, 6.62%. Found: C, 87.27; H, 6.78%.

Salt **1c**: hygroscopic glassy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.96–3.07 (m, CH_2), 4.09–4.19 (m, CH_2), 7.03 (d, 2H, $J = 8.0$ Hz, ClC_6H_4), 7.15 (d, 2H, $J = 8.0$ Hz, ClC_6H_4), 7.60–7.89 (m, 15H, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.76 (d, $J_{PC} = 48$ Hz, CH_2), 28.01 (d, $J_{PC} = 2$ Hz, CH_2), 118.23 (d, $J_{PC} = 85$ Hz, PPh_3), 129.06 (ClC_6H_4), 130.46 (ClC_6H_4), 130.76 (d, $J_{PC} = 13$ Hz, PPh_3), 133.02 (ClC_6H_4), 134.01 (d, $J_{PC} = 10$ Hz, PPh_3), 135.35 (d, $J_{PC} = 3$ Hz, PPh_3), 136.92 (d, $J_{PC} = 14$ Hz, ClC_6H_4). Salt **7c**: colorless crystals. mp 203–205 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.52–2.61 (m, 2H, CH_2), 2.62–2.76 (m, 2H, CH_2), 6.71 (d, 2H, $J = 8.0$ Hz, ClC_6H_4), 6.79–6.84 (m, 4H, BPh_4), 6.90–6.96 (m, 8H, BPh_4), 7.11 (d, 2H, $J = 8.0$ Hz, ClC_6H_4), 7.20–7.28 (m, 6H, PPh_3), 7.41 (br, 8H, BPh_4), 7.50–7.80 (m, 6H, PPh_3), 7.72–7.80 (m, 3H, PPh_3). ^{13}C NMR (100 MHz, CD_3SOCD_3): δ 22.20 (d, $J_{PC} = 48$ Hz, CH_2), 27.45 (CH_2), 118.71 (d, $J_{PC} = 86$ Hz, PPh_3), 122.23 (BPh_4), 125.98 (BPh_4), 129.05 (ClC_6H_4), 130.86 (ClC_6H_4), 130.92 (d, $J_{PC} = 13$ Hz, PPh_3), 132.12 (ClC_6H_4), 134.22 (d, $J_{PC} = 10$ Hz, PPh_3), 135.64 (PPh_3), 136.17 (BPh_4), 138.38 (d, $J_{PC} = 17$ Hz, ClC_6H_4), 163.97 (q, $J_{BC} = 49$ Hz, BPh_4). Anal. Calcd for $C_{50}H_{43}BClP$: C, 83.28; H, 6.01%. Found: C, 83.24; H, 6.30%.

Salt **1d**: hygroscopic glassy solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95–3.09 (m, 2H, CH_2), 4.22–4.34 (m, 2H, CH_2), 7.23–7.30 (m, 4H, BrC_6H_4), 7.60–7.95 (m, 15H, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.11 (d, $J_{PC} = 48$ Hz, CH_2), 27.70 (CH_2), 117.66 (d, $J_{PC} = 86$ Hz, PPh_3), 120.60 (BrC_6H_4), 130.59 (d, $J_{PC} = 12$ Hz, PPh_3), 130.70 (BrC_6H_4), 131.59 (BrC_6H_4), 133.65 (d, $J_{PC} = 11$ Hz, PPh_3), 135.20 (d, $J_{PC} = 2$ Hz, PPh_3), 137.28 (d, $J_{PC} = 15$ Hz, BrC_6H_4). Salt **7d**: colorless crystals, mp 211–212 °C, ^{1}H NMR (400 MHz, CD_3SOCD_3): δ 2.70–2.86 (m, 2H, CH_2), 3.80–3.90 (m, 2H, CH_2), 6.70–6.78 (m, 4H, BPh_4), 6.80–6.90 (m, 8H, BPh_4), 7.14 (br, 8H, BPh_4), 7.21 (d, 2H, $J = 8.0$ Hz, BrC_6H_4), 7.45 (d, 2H, $J = 8.0$ Hz, BrC_6H_4), 7.65–7.90 (m, 15H, PPh_3). ^{13}C NMR (100 MHz, CD_3SOCD_3): δ 22.12 (d, $J_{PC} = 49$ Hz, CH_2), 27.55 (CH_2), 118.77 (d, $J_{PC} = 86$ Hz, PPh_3), 120.60 (BrC_6H_4), 122.26 (BPh_4), 126.02 (BPh_4), 130.97 (d, $J_{PC} = 12$ Hz, PPh_3), 131.31 (BrC_6H_4), 132.02 (BrC_6H_4), 134.29 (d, $J_{PC} = 10$ Hz, PPh_3), 135.66 (PPh_3), 136.20 (BPh_4), 138.90 (d, $J_{PC} = 17$ Hz, BrC_6H_4), 164.00 (q, $J_{BC} = 49$ Hz, BPh_4). Anal. Calcd for $C_{50}H_{43}BBrP$: C, 78.44; H, 5.66%. Found: C, 78.40; H, 5.87%.

Salt **1e**: hygroscopic glassy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09–3.22 (m, 2H, CH_2), 4.31–4.42 (m, 2H, CH_2), 7.48–7.59 (m, 4H, $CF_3C_6H_4$), 7.60–7.95 (m, 15H, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.30 (d, $J_{PC} = 50$ Hz, CH_2), 28.20 (d, $J_{PC} = 3$ Hz, CH_2), 117.79 (d, $J_{PC} = 86$ Hz, PPh_3), 124.18 (q, $J_{CF} = 270$ Hz, CF_3), 125.63 (d, $J_{PC} = 4$ Hz, $CF_3C_6H_4$), 129.02 (d, $J_{CF} = 32$ Hz, $CF_3C_6H_4$), 129.42 ($CF_3C_6H_4$), 130.72 (d, $J_{PC} = 13$ Hz, PPh_3), 133.80 (d, $J_{PC} = 11$ Hz, PPh_3), 135.36 (d, $J_{PC} = 3$ Hz, PPh_3), 142.41 (d, $J_{PC} = 14$ Hz, $CF_3C_6H_4$). Salt **7e**: colorless solid; mp 188–190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48–2.58 (m, 2H, CH_2), 2.65–2.80 (m, 2H, CH_2), 6.75–6.97 (m, 14H, BPh_4), 7.20–7.28 (m, 6H, PPh_3 and $CF_3C_6H_4$), 7.34–7.43 (m, 10H, BPh_4 and $CF_3C_6H_4$), 7.48–7.58 (m, 6H, PPh_3), 7.70–7.79 (m, 3H, PPh_3). ^{13}C NMR (100 MHz, CD_3SOCD_3): δ 22.01 (d, $J_{PC} = 49$ Hz, CH_2), 27.90 (CH_2), 118.64 (d, $J_{PC} = 85$ Hz, PPh_3), 122.27 (BPh_4), 124.92 (q, $J_{CF} = 270$ Hz, CF_3), 125.99 ($CF_3C_6H_4$), 126.02 (BPh_4), 128.23 (q, $J_{CF} = 32$ Hz, $CF_3C_6H_4$), 129.90 ($CF_3C_6H_4$), 130.97 (d, $J_{PC} = 12$ Hz, PPh_3), 134.23 (d, $J_{PC} = 10$ Hz, PPh_3), 135.68 (PPh_3), 136.20 (BPh_4), 144.24 (d, $J_{PC} = 17$ Hz, $CF_3C_6H_4$), 164.00 (q, $J_{BC} = 49$ Hz, BPh_4). Anal. Calcd for $C_{51}H_{43}BF_3P$: C, 81.17; H, 5.74%. Found: C, 80.92; H, 6.01%.

Synthesis of 1c from *p*-Chlorostyrene. A mixture of triphenylphosphine (0.68 g, 2.6 mmol) and hydrobromic acid (48% in water, 0.34 mL, 2.0 mmol) was heated to 130 °C for 5 min. *p*-Chlorostyrene (**3c**) (0.31 g, 2.2 mmol) was added to the mixture and heated to 270 °C for 50 min. The reaction mixture was cooled to rt. The obtained pale brown glassy solid was dissolved in di-

chloromethane, washed with aq. sodium carbonate, extracted with dichloromethane, dried over magnesium sulfate and filtered, and the solvent was evaporated to give pale yellow glassy solid of crude **1c** (0.60 g, 1.24 mmol).

Synthesis of Salt 1f from *o*-Methylstyrene (3f). A mixture of triphenylphosphine (0.68 g, 2.6 mmol) and hydrobromic acid (48% in water, 0.34 mL, 2.0 mmol) was heated to 130 °C for 5 min, and then *o*-methylstyrene (**3f**) (0.25 g, 2.1 mmol) was added. The reaction mixture was heated to 270 °C for 30 min. The reaction mixture was cooled to rt and washed with hexane (5 mL × 3). The remaining solid afforded glassy solid 2-(*o*-tolyl)ethyltriphenylphosphonium bromide (**1f**). Salt **1f**: glaasy solid. Salt **1f**: hygroscopic glassy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 3H, Me), 2.95–3.06 (m, 2H, CH_2), 4.05–4.18 (m, 2H, CH_2), 7.02–7.29 (m, 4H, *o*-Tol), 7.65–7.93 (m, 15H, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.44 (Me), 23.83 (d, $J_{PC} = 47$ Hz, CH_2), 25.32 (CH_2), 117.79 (d, $J_{PC} = 85$ Hz, PPh_3), 126.61 (*o*-Tol), 127.25 (*o*-Tol), 129.28 (*o*-Tol), 130.51 (*o*-Tol), 130.72 (d, $J_{PC} = 12$ Hz, PPh_3), 133.67 (d, $J_{PC} = 10$ Hz, PPh_3), 135.37 (d, $J_{PC} = 2$ Hz, PPh_3), 135.57 (*o*-Tol), 136.44 (d, $J_{PC} = 14$ Hz, *o*-Tol). Salt **1f** was changed to the corresponding tetraphenylborate **7f**: colorless solid (0.87 g, 1.24 mmol), mp 169–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H, CH_3), 2.75–2.89 (m, 4H, CH_2), 6.76–6.93 (m, 12H, BPh_4 and *o*-Tol), 7.05–7.19 (m, 3H, *o*-Tol), 7.23–7.36 (m, 15H, PPh_3 and BPh_4), 7.48–7.57 (m, 6H, PPh_3), 7.70–7.78 (m, 3H, PPh_3). ^{13}C NMR (100 MHz, CD_3SOCD_3): δ 19.30 (CH_3), 21.89 (d, $J_{PC} = 47$ Hz, CH_2), 25.41 (d, $J_{PC} = 3$ Hz, CH_2), 118.88 (d, $J_{PC} = 85$ Hz, PPh_3), 122.27 (BPh_4), 126.02 (BPh_4), 126.88 (*o*-Tol), 127.69 (*o*-Tol), 129.49 (*o*-Tol), 130.94 (*o*-Tol), 130.94 (d, $J_{PC} = 13$ Hz, PPh_3), 134.31 (d, $J_{PC} = 10$ Hz, PPh_3), 135.67 (d, $J_{PC} = 3$ Hz, PPh_3), 136.20 (BPh_4), 136.35 (*o*-Tol), 137.86 (d, $J_{PC} = 16$ Hz, *o*-Tol), 164.01 (q, $J_{BC} = 49$ Hz, BPh_4). Anal. Calcd for $C_{51}H_{48}BOP$: C, 85.23; H, 6.73%. Found: C, 85.14; H, 6.55%.

Salt **1g** and **7g** were obtained in a similar manner. Salt **1g**: hygroscopic glassy solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.13–3.22 (m, 2H, CH_2), 4.05–4.18 (m, 2H, CH_2), 7.10–7.25 (m, 2H, *o*-ClC_6H_4), 7.30–7.55 (m, 2H, *o*-ClC_6H_4), 7.65–8.05 (m, 15H, PPh_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.33 (d, $J_{PC} = 48$ Hz, CH_2), 26.05 (d, $J_{PC} = 2$ Hz, CH_2), 117.67 (d, $J_{PC} = 85$ Hz, PPh_3), 127.77 (ClC_6H_4), 128.86 (ClC_6H_4), 129.38 (ClC_6H_4), 130.72 (d, $J_{PC} = 13$ Hz, PPh_3), 131.91 (ClC_6H_4), 133.0 (ClC_6H_4), 133.78 (d, $J_{PC} = 11$ Hz, PPh_3), 135.43 (d, $J_{PC} = 3$ Hz, PPh_3), 135.71 (ClC_6H_4). Salt **7g**: colorless solid. mp 157–159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75–2.92 (m, 4H, CH_2CH_2), 6.75–6.83 (m, 4H, BPh_4), 6.85–6.91 (m, 9H, *o*-ClC_6H_4 + BPh_4), 7.09 (t, 1H, $J = 7.6$ Hz, *o*-ClC_6H_4), 7.19 (t, 1H, $J = 7.6$ Hz, *o*-ClC_6H_4), 7.31–7.40 (m, 15H, BPh_4, PPh_3, and *o*-ClC_6H_4), 7.53–7.60 (m, 6H, PPh_3), 7.73–7.80 (m, 3H, PPh_3). ^{13}C NMR (100 MHz, CD_3SOCD_3): δ 21.49 (d, $J_{PC} = 49$ Hz, CH_2), 25.96 (CH_2), 118.64 (d, $J_{PC} = 85$ Hz, PPh_3), 122.26 (BPh_4), 126.00 (BPh_4), 128.24 (ClC_6H_4), 129.68 (ClC_6H_4), 130.05 (ClC_6H_4), 130.96 (d, $J_{PC} = 12$ Hz, PPh_3), 131.48 (ClC_6H_4), 133.35 (ClC_6H_4), 134.30 (d, $J_{PC} = 10$ Hz, PPh_3), 135.74 (PPh_3), 136.22 (BPh_4), 136.93 (d, $J_{PC} = 16$ Hz, ClC_6H_4), 164.10 (q, $J_{BC} = 49$ Hz, BPh_4). Anal. Calcd for $C_{50}H_{43}BClP$: C, 83.28; H, 6.01%. Found: C, 83.45; H, 6.08%.

Thermolysis of 1-Indanyltriphenylphosphonium Bromide (2i). Phosphonium bromide **2i** (0.076 g, 0.17 mmol) was heated at 275 °C for 20 min. The reaction mixture was cooled to rt and extracted with hexane (3 × 5 mL). The combined extracts were concentrated to afford indene (0.013 g, 0.11 mmol), which was identical to the authentic sample. The remaining solid was mainly triphenylphosphonium bromide (0.045 g, 0.13 mmol).

Synthesis of Deuterated Phosphonium Salt 1-D-2c. To a solution of *p*-chloroacetophenone (0.772 g, 5.0 mmol) in THF (10 mL) was added lithium alminum deuteride (0.215 g, 5.0 mmol) in one portion. After refluxing for 13 h, the reaction mixture was poured into water, and the solution was extracted with dichloromethane (30 mL) for three times. The combined extracts were dried over magnesium sulfate, filtered, and concentrated to afford 1-*p*-chlorophenyl-1-deuteroethyl alcohol (1.00 g, 5.0 mmol) in 100% yield. This alcohol (0.157 g, 1.0 mmol) was treated with triphenylphosphine (0.343 g, 1.0 mmol) and 47% HBr (0.194 g, 1.2 mmol) at 170 °C for 2 h. The cooled reaction mixture was recrystallized from 2-propanol to afford phosphonium bromide D-**2c** (0.346 g, 0.85 mmol) in 85% yield. 1-(*p*-chlorophenyl)-1-deuteroethyl alcohol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 3H, Me), 7.31 (s, 4H, Ar). 1-*p*-Chlorophenyl-1-deutero-ethylphosphonium bromide (1-**D**-2c); mp 230–232 °C (lit.[8] mp 230–232 °C) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72 (d, 3H, $J_{PH} = 35$ Hz, Me), 7.12 (d, 2H, $J = 8$ Hz, Ar), 7.20 (d, 2H, $J = 8$ Hz, Ar), 7.60–7.93 (m, 15H, Ph).

Thermal Rearrangement of 1-D-2c. A mixture of Salt 1-D-**2c** (0.242 g, 0.5 mmol) and triphenylphosphine (0.065 g, 0.25 mmol) was heated at 260 °C for 30 min. The cooled reaction mixture was dissolved in acetone (5 mL), which was added to a solution of sodium tetraphenylborate (0.171 g, 0.5 mmol) in acetone (5 mL). The precipitates were removed by filtration, and the solvent was evaporated to give pale brown oily crystals, which were washed with ether (3 mL × 3) and recrystallized from acetone–ether to afford colorless crystals of deuterated salt of **1c** (0.180 g, 0.25 mmol). Mp 197–199 °C. ^{1}H NMR spectrum of deuterated **1c** was identical to that of **1c** except for the integral ratio of methylene signals. The NMR spectrum (in $CDCl_3$) showed two methylenes at 4.26 and 3.05 in 58:42 ratio.

Synthesis of *p*-(Chlorophenyl)ethene-2-^{13}C (2-^{13}C-3c). To a solution of ^{13}C-methyltriphenylphosphonium iodide (0.406 g, 1.0 mmol) and DBU (0.175 g, 1.1 mmol) in dichloromethane (10 mL) was added *p*-chlorobenzaldehyde (0.090 g, 0.6 mmol) in one-portion. After refluxing for 12 h, the reaction mixture was washed with water (5 mL × 3), separated, dried over magnesium sulfate, and concentrated to afford a colorless oil. Chromatography on silica gel by elution from hexane gave 2-^{13}C-enriched **3c** (*p*-$ClC_6H_4CH = {}^{13}CH_2$, 2-^{13}C-**3c**) (0.067 g, 0.048 mmol). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.27 (dd, 1H, $J = 11$ Hz, $J_{CH} = 161$ Hz, $=CH_2$), 5.72 (dd, 1H, $J = 17$ Hz, $J_{CH} = 159$ Hz, $=CH_2$), 6.66 (dd, 1H, $J = 11$ and 17 Hz, =CH), 7.29 (d, 2H, $J = 8$ Hz, Ar), 7.32 (d, 2H, $J = 8$ Hz, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.53 ($={}^{13}CH_2$), 127.53 (Ar), 128.76 (Ar), 133.86 (Ar), 135.38 (=CHAr), 136.08 (Ar).

Reaction of *p*-Chloro-2-^{13}C-styrene (2-^{13}C-3C) with Triphenylphosphonium Bromide. To a mixture of triphenylphosphonium bromide and triphenylphosphine was added 2-^{13}C-**3c** (0.060 g, 0.43 mmol) at 130 °C and the temperature was up to 265 °C for 30 min. After the mixture was cooled to rt, the reaction mixture was extracted with hexane and ether. In the ^{1}H NMR spectrum of the mixture, peaks for triphenylphosphine, 1-(*p*-chlorophenyl)ethyl-2-^{13}C-triphenylphosphonium bromide (2-^{13}C-**2c**), and 2-(*p*-chlorophenyl)ethyl-1-^{13}C-triphenylphosphonium bromide (1-^{13}C-**1c**) were observed. ^{13}C NMR clearly shows the existence of 2-^{13}C-**2c** (δ 17.14) and 1-^{13}C-**1c** (δ 24.77) in almost an 1:4 ratio. No peaks assigned to 1-*p*-chlorophenyl-1-^{13}C-ethyltriphenylphosphonium bromide were observed.

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