Onium Transfer Reaction of (*β*,*β*-Dialkylvinyl)(phenyl)iodonium Tetrafluoroborates via an Alkylidene Carbene Pathway: Synthesis of Group 15 Alkenyl(triphenyl)- and Group 16 Alkenyl(diphenyl)onium Salts

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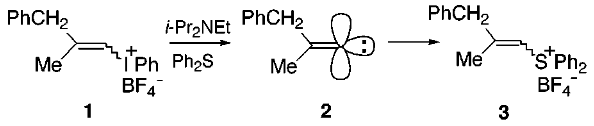
Group 15 1-alkenyl(triphenyl)onium (P, As, Sb) tetrafluoroborates were prepared via an onium transfer reaction of alkenyl(phenyl)iodonium tetrafluoroborates under mild conditions. The reaction involves base-induced reductive α-elimination of the iodonium salts, followed by nucleophilic trapping of the resulting free alkylidene carbenes with group 15 element-centered nucleophiles. The onium transfer reaction of the alkenyliodonium salts also produced group 16 1-alkenyl(diphenyl)onium (S, Se, Te) tetrafluoroborates in good yields.

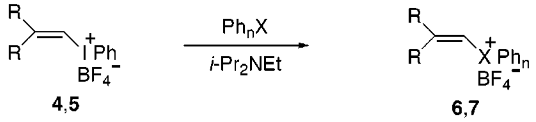
Base treatment of 1-alkenyl(phenyl)iodonium tetrafluoroborates under mild conditions leads to reductive α-elimination of iodobenzene to generate alkylidene carbenes, because of the very high leaving group ability of the phenyliodonio group.[1,2] We reported that the alkenyl group of (*E*)- and (*Z*)-1-alkenyl(phenyl)iodonium tetrafluoroborates **1** was selectively transferred to diphenyl sulfide by reaction with diisopropylethylamine to give a mixture of stereoisomers of the alkenylsulfonium salt **3** (Scheme 1).[3] The high degree of stereoconvergence of the olefin geometry in this onium transfer reaction confirmed the involvement of free alkylidene carbene **2** via base-induced reductive α-elimination.

Complete stereoconvergence for intramolecular 1,5-carbon−hydrogen insertions of alkenyliodonium salts yielding cyclopentenes[1a] and a small Hammett ρ value (−0.56) for the cycloaddition reaction of the alkenyliodonium salt **4** to ring-substituted styrenes[4] also suggests the intermediacy of a free alkylidene carbene rather than a carbenoid. We report herein a new method for synthesis of group 15 alkenyl(triphenyl)- and group 16 alkenyl(diphenyl)onium tetrafluoroborates that involves an onium transfer reaction of alkenyl(phenyl)iodonium tetrafluoroborates **4** and **5** under mild conditions via the intervention of free alkylidene carbenes. In this reaction, 1-alkenyl groups of the iodonium salts **4** and **5** were selectively transferred in preference to the phenyl group to group 15 and 16 element-centered nucleophiles (Scheme 2).

Scheme 1



Scheme 2



4,**6**: R = Me; **5**,**7**: R,R = $(CH_2)_5$
Ph_nX = Ph_3N, Ph_3P, Ph_3As, Ph_3Sb, Ph_3Bi, Ph_2O, Ph_2S, Ph_2Se, Ph_2Te

No onium transfer between 2-methyl-1-propenyl(phenyl)iodonium tetrafluoroborate (**4**) and triphenylamine via alkylidene carbene intermediates was observed; however, use of triphenylphosphine as a nucleophile results in the formation of alkenyl(triphenyl)phosphonium tetrafluoroborate **6b**. Thus, exposure of the iodonium salt **4** to 1.2 equiv of triphenylphosphine in the presence of diisopropylethylamine (1.2 equiv) in dichloromethane at room temperature allows the onium transfer reaction to proceed, yielding the alkenylphosphonium salt **6b** in 56% yield (Table 1, entry 2). Triphenylarsine and triphenylstibine also react with 2-methyl-1-propenylidene generated from the reaction of the iodonium salt **4** with diisopropylethylamine to give under similar conditions the alkenylarsonium **6c** and alkenylstibonium salts **6d** in 52% and 44% yields, respectively. The lowest homologue of the trivalent group 15 compound, triphenylbismuthine, shows low nucleophilicity compared to triphenylphosphine, -arsine, and -stibine[5] and, in fact, was recovered unchanged in the reaction with **4**. Use of excess amounts (2 equiv) of As and Sb nucleophiles increased the yields of the arsonium **6c** and the stibonium salts **6d** (Table 1, entries 4 and 6). Reaction of the

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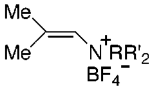
Table 1. Synthesis of Group 15 Alkenyl(triphenyl)onium Tetrafluoroborates[a]

entry	iodonium salt	Ph_3X	product	% yield[b]
1	**4**	Ph_3N[c]	**6a**	0
2	**4**	Ph_3P	**6b**	56 (70)
3	**4**	Ph_3As	**6c**	52 (74)
4	**4**	Ph_3As[d]	**6c**	69
5	**4**	Ph_3Sb	**6d**	44 (54)
6	**4**	Ph_3Sb[d]	**6d**	70
7	**4**	Ph_3Bi	**6e**	0
8	**5**	Ph_3P	**7b**	85
9	**5**	Ph_3As	**7c**	80
10	**5**	Ph_3Sb	**7d**	83

[a] Reactions were carried out using diisopropylethylamine (1.2 equiv) and Ph_3X (1.2 equiv) in CH_2Cl_2 at room temperature for 15 min under N_2. [b] Isolated yields. Yields in parentheses were determined by ^{1}H NMR. [c] 1.5 h at room temperature. [d] Ph_3X (2 equiv).

cyclohexylidenemethyliodonium tetrafluoroborate **5** with triphenylphosphine, -arsine and -stibine afforded a higher yield (more than 80%) of the alkenylonium salts **7b**−**d**.

Low reactivity of triphenylamine toward 2-methyl-1-propenylidene can be attributed to a large steric demanding of the amine, evoked probably by the small atomic size of nitrogen. In fact, reaction of **4** with 2.5 equiv of triethylamine gave the alkenylammonium salt **8** in 56% yield, whereas with the more sterically demanding diisopropylethylamine no formation of the onium transfer product **9** was observed. An alternative explanation might involve the low polarity of triphenylamine. The dipole moment of the triphenyl derivatives of group 15 elements is as follows: NPh_3 (0.26 D), PPh_3 (1.45 D), $AsPh_3$ (1.07 D), $SbPh_3$ (0.57 D), $BiPh_3$ (0 D).[6] The donor ability toward silver perchlorate in dimethyl sulfoxide largely follows the pattern of polarity.[5d]



8: R = R' = Et
9: R = Et, R' = *i*-Pr

1,2-Migration of α-aryl groups of alkylidene carbene is a low-energy process and proceeds rapidly.[7] We found that attempts at nucleophilic trapping of the alkylidene carbene **11** with triphenylarsine to lead to onium transfer cannot compete with the facile 1,2-aryl migration: thus, the reaction of β,β-diphenylvinyliodonium tetrafluoroborate **10** with triphenylarsine in the presence of diisopropylethylamine in dichloromethane at 0 °C exclusively results in the 1,2-phenyl migration and affords diphenylacetylene (**12**) quantitatively with no signs for formation of the onium transfer product **13** (Scheme 3). Interestingly, however, 2,2-diphenylvinylarsonium tetrafluoroborate **13** was produced in 67% yield when the reaction was carried out in acetonitrile, without using a base, at 50 °C for 6 h. This nucleophilic vinylic substitution does not proceed at room temperature. One or more of the following reaction mechanisms explains the formation of the 2,2-diphenylvinylarsonium salt **13**: (1) a direct in-plane vinylic S_N2 substitution,[8] (2) an ionic mechanism through vinylenebenzenium ion intermediate,[9] (3) ligand coupling on hypervalent iodine(III).[10]

Scheme 3

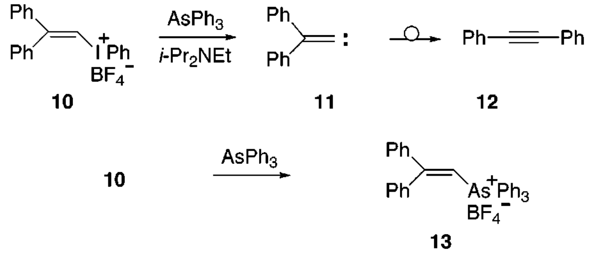


Table 2. Synthesis of Group 16 Alkenyl(diphenyl)onium Tetrafluoroborates[a]

entry	iodonium salt	Ph_2X	product	% yield[b]
1	**4**	Ph_2O[c]	**6f**	0
2	**4**	Ph_2S	**6g**	60 (70)
3	**4**	Ph_2S[d]	**6g**	67 (92)
4	**4**	Ph_2Se	**6h**	54 (70)
5	**4**	Ph_2Te	**6i**	68 (99)
6	**5**	Ph_2S	**7g**	67
7	**5**	Ph_2Se	**7h**	75
8	**5**	Ph_2Te	**7i**	89

[a] Reactions were carried out using diisopropylethylamine (1.2 equiv) and Ph_2X (1.2 equiv) in CH_2Cl_2 at room temperature for 15 min under N_2. [b] Isolated yields. Yields in parentheses were determined by ^{1}H NMR. [c] 1 h at room temperature. [d] Ph_2S (2 equiv).

Results of the reaction of the diphenyl derivatives of group 16 nucleophiles with the free alkylidene carbenes are summarized in Table 2. Here again, no onium transfer reaction between the iodonium salt **4** and the diphenyl derivative of a second-row element, diphenyl ether, was observed; however, diphenyl sulfide undergoes clean onium transfer reactions via alkylidene carbene intermediates and affords the alkenyl(diphenyl)sulfonium salt **6g** in 60% yield (Table 2, entry 2). Similarly, alkenyl(diphenyl)selenonium **6h** and **7h** and alkenyl(diphenyl)telluronium tetrafluoroborates **6i** and **7i** were prepared via the onium transfer reaction in good yields. Except for alkenyl(triphenyl)phosphonium salts, synthetic methods for producing other triphenylonium salts of group 15 elements and of diphenylonium salts of group 16 elements are very limited.[11,12] The present methodology used for the onium transfer reaction via an alkylidene carbene intermediate provides a new and convenient route for the synthesis of β,β-dialkylvinylonium salts of group 15 and 16 elements.

The parent ethenyl(triphenyl)phosphonium and ethenyl(triphenyl)arsonium salts act as good Michael acceptors toward carbon nucleophiles, i.e., enolate anions and lithium dialkyl cuprates.[11] Introduction of alkyl substit-

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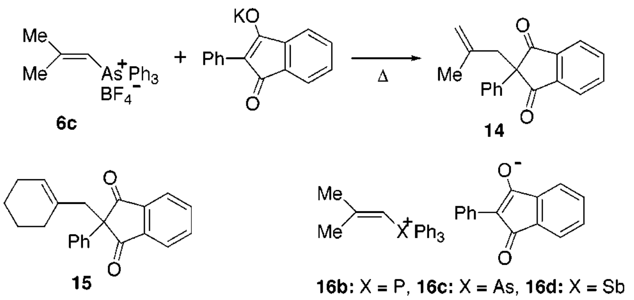
Scheme 4



uents at their β positions will decrease the reactivity toward the Michael additions because of the increased steric hindrance. Thus, the reaction of 2-methyl-1-propenylarsonium salt **6c** with the potassium enolate derived from 2-phenyl-1,3-indandione in refluxing dichloromethane−THF (1:2) results in allylation instead of Michael addition, giving the diketone **14** in 85% yield. At room temperature, the reaction afforded the onium enolate **16c** (85%) via a ligand exchange. Similarly, the arsonium salt **7c** gave the allylation product **15** (83%) in refluxing dichloromethane−THF. The allylation probably proceeds via the base-catalyzed isomerization of the vinylarsonium salts **6c** and **7c** to the allylarsonium salts. Neither allylation nor Michael addition were observed in the reactions of the phosphonium **6b** and stibonium salts **6d** with the enolate under the same conditions (in refluxing dichloromethane−THF); these reactions gave the onium enolates **16b,d** in good yields (Scheme 4).

The structure of **16c** was established by a single-crystal X-ray analysis.[13] The ORTEP representation of Figure 1 clearly illustrates an ionic structure; the arsine has a tetrahedral geometry with the bond angles C−As−C 107.6(4)−110.9(4)° and the bond lengths 1.87(1)−1.95(1) Å. All the atoms attached to the carbon−carbon double bond are in the same plane, and the bond length of C19−C20 is 1.34(2) Å.

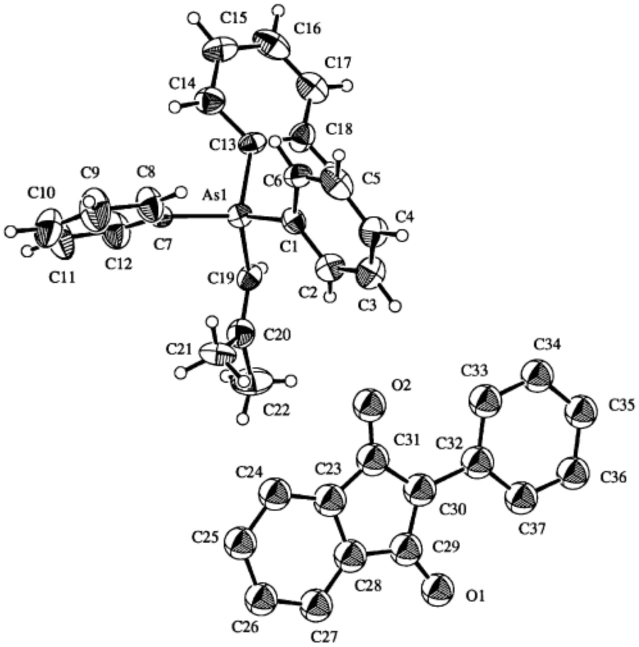


Figure 1. ORTEP representation of the arsonium enolate **16c**.

Experimental Section

General Methods. For general experimental details, see ref 2. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Kieselgel 60 (Merck, 230−400 mesh) was used for flash chromatography. 2-Methyl-1-propenyl(phenyl)iodonium tetrafluoroborate (**4**) was prepared by tin−iodonium exchange reaction of 2-methyl-1-(trimethylstannyl)prop-1-ene with iodosylbenzene in the presence of $BF_3\cdot Et_2O$.[4]

Synthesis of (Cyclohexylidenemethyl)(phenyl)iodonium Tetrafluoroborate (5). (Cyclohexylidenemethyl)trimethylsilane was prepared according to the procedure described previously.[14] To a stirred suspension of iodosylbenzene (487 mg, 2.2 mmol) and the vinylsilane (232 mg, 1.4 mmol) in dichloromethane (20 mL) was added dropwise $BF_3\cdot Et_2O$ (313 mg, 2.2 mmol) at 0 °C in nitrogen, and the mixture was stirred for 1 h at 0 °C. After the addition of a saturated aqueous solution of sodium tetrafluoroborate (3.0 g, 28 mmol), the mixture was stirred for 15 min. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation at −78 °C. Recrystallization from dichloromethane−diethyl ether−hexane gave the iodonium salt **5** (255 mg, 48%) as colorless needles: mp 97−98 °C; IR (KBr) 1609, 1443, 1060 (br), 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 6.67 (s, 1H), 2.58−2.53 (m, 4H), 1.72−1.53 (m, 6H); HRMS (FAB) calcd for $C_{13}H_{16}I$ [(M − BF_4)$^+$] 299.0297, found 299.0270. Anal. Calcd for $C_{13}H_{16}BF_4I$: C, 40.45; H, 4.18. Found: C, 40.15; H, 4.37.

Synthesis of 2,2-Diphenylethenyl(phenyl)iodonium Tetrafluoroborate (10). To a stirred solution of 1-bromo-2,2-diphenylethene[15] (900 mg, 3.5 mmol) in THF (30 mL) was added 1.43 M *tert*-butyllithium solution in pentane (5.1 mL, 7.3 mmol) dropwise at −78 °C in argon, and the mixture was stirred for 2 h. Trimethyl borate (361 mg, 3.5 mmol) was added, and the mixture was stirred at −78 °C for 1 h and at 0 °C for 1 h. After the addition of a 10% aqueous HCl solution (30 mL) at 0 °C, the mixture was stirred for 1 h. The mixture was extracted with diethyl ether, and the combined organic phase

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was washed with water and brine and dried over anhydrous Na_2SO_4. Concentration under aspirator vacuum gave (2,2-diphenyl-1-ethenyl)boronic acid, which was used without further purification. To a stirred solution of the crude vinylboronic acid in dichloromethane (5 mL) was added dropwise $BF_3{\cdot}Et_2O$ (595 mg, 4.2 mmol) at 0 °C in nitrogen, and the mixture was stirred for 10 min at 0 °C. After the addition of a solution of diacetoxyiodobenzene (1.4 g, 4.2 mmol) in dichloromethane (5 mL), the mixture was stirred for 30 min at 0 °C. A saturated aqueous solution of sodium tetrafluoroborate (7.7 g, 70 mmol) was added, and the mixture was stirred for 15 min. Extraction with dichloromethane, filtration, washing with water, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane and diethyl ether by decantation at −78 °C to give the vinyliodonium salt **10** (1.41 g, 86%). Further purification of the iodonium salt by recrystallization from dichloromethane−diethyl ether−hexane gave colorless needles: mp 125−126 °C dec; IR (KBr) 1579, 1060 (br), 740, 700 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ 8.09 (s, 1H), 8.00 (d, $J = 7.5$ Hz, 2H), 7.76 (t, $J = 7.5$ Hz, 1H), 7.68−7.30 (m, 12H); HRMS (FAB) calcd for $C_{20}H_{16}I$ [$(M - BF_4)^+$] 383.0297, found 383.0314. Anal. Calcd for $C_{20}H_{16}BF_4I$: C, 51.10; H, 3.43. Found: C, 50.86; H, 3.63.

General Procedure for Synthesis of Group 15 Alkenyl(triphenyl)onium Tetrafluoroborates 6 and 7 (Table 1). To a stirred solution of an alkenyl(phenyl)iodonium tetrafluoroborate (0.1 mmol) and a group 15 heteroatom nucleophile (Ph_3X, 0.12 mmol) in dichloromethane (1 mL) was added dropwise diisopropylethylamine (16 mg, 0.12 mmol) under nitrogen at room temperature, and the mixture was stirred for 15 min. After addition of water, the mixture was extracted with dichloromethane. Filtration and concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation to give the group 15 onium salt. Further purification of the onium salt was accomplished by recrystallization from dichloromethane−hexane.

(2-Methyl-1-propenyl)triphenylphosphonium tetrafluoroborate (6b): colorless plates; mp 244−245 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1616, 1060 (br), 751, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84−7.60 (m, 15H), 6.24 (d, $^2J_{PH} = 23.2$ Hz, 1H), 2.37 (s, 3H), 1.74 (d, $^4J_{PH} = 2.3$ Hz, 3H); HRMS (FAB) calcd for $C_{22}H_{22}P$ [$(M - BF_4)^+$] 317.1458, found 317.1443. Anal. Calcd for $C_{22}H_{22}BF_4P$: C, 64.73; H, 5.43. Found: C, 64.76; H, 5.28.

(2-Methyl-1-propenyl)triphenylarsonium tetrafluoroborate (6c): colorless crystals; mp 206−208 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1623, 1060 (br), 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78−7.62 (m, 15H), 6.22 (br s, 1H), 2.33 (d, $J = 0.9$ Hz, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 134.2, 132.2, 131.2, 122.5, 103.6, 28.4, 24.9; HRMS (FAB) calcd for $C_{22}H_{22}As$ [$(M - BF_4)^+$] 361.0937, found 361.0944. Anal. Calcd for $C_{22}H_{22}AsBF_4$: C, 58.96; H, 4.95. Found: C, 58.68; H, 4.96.

(2-Methyl-1-propenyl)triphenylstibonium tetrafluoroborate (6d): colorless prisms; mp 172−174 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1609, 1060 (br), 748 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.83−7.57 (m, 15H), 6.26 (br s, 1H), 2.29 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 134.8, 133.6, 131.2, 122.2, 102.8, 28.0, 27.3; HRMS (FAB) calcd for $C_{22}H_{22}Sb$ [$(M - BF_4)^+$] 407.0760, found 407.0786. Anal. Calcd for $C_{22}H_{22}BF_4Sb$: C, 53.39; H, 4.48. Found: C, 53.06; H, 4.45.

(Cyclohexylidenemethyl)triphenylphosphonium tetrafluoroborate (7b): pale yellow crystals; mp 182−183 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1610, 1060 (br), 743, 720 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.95−7.50 (m, 15H), 6.15 (d, $^2J_{PH} = 24.0$ Hz, 1H), 2.69 (t, $J = 5.7$ Hz, 2H), 2.15−1.97 (m, 2H), 1.87−1.70 (m, 2H), 1.64−1.45 (m, 2H), 1.40−1.20 (m, 2H); HRMS (FAB) calcd for $C_{25}H_{26}P$ [$(M - BF_4)^+$] 357.1772, found 357.1789. Anal. Calcd for $C_{25}H_{26}BF_4P$: C, 67.59; H, 5.90. Found: C, 67.34; H, 5.79.

(Cyclohexylidenemethyl)triphenylarsonium tetrafluoroborate (7c): pale yellow crystals; mp 168−172 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1621, 1060 (br), 749 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.81−7.63 (m, 15H), 6.12 (s, 1H), 2.76 (t, $J = 6.1$ Hz, 2H), 2.11 (t, $J = 6.1$ Hz, 2H), 1.91−1.74 (m, 2H), 1.61−1.50 (m, 2H), 1.42−1.23 (m, 2H); HRMS (FAB) calcd for $C_{25}H_{26}As$ [$(M - BF_4)^+$] 401.1250, found 401.1260. Anal. Calcd for $C_{25}H_{26}AsBF_4$: C, 61.51; H, 5.37. Found: C, 61.74; H, 5.41.

(Cyclohexylidenemethyl)triphenylstibonium tetrafluoroborate (7d): colorless prisms; mp 140−141 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1601, 1437, 1060 (br), 744, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.7−7.59 (m, 15H), 6.28 (s, 1H), 2.65 (t, $J = 6.2$ Hz, 2H), 2.22 (t, $J = 6.2$ Hz, 2H), 1.83−1.74 (m, 2H), 1.62−1.51 (m, 2H), 1.51−1.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 134.8, 133.5, 131.1, 122.6, 99.6, 38.8, 28.0, 27.8, 24.8; HRMS (FAB) calcd for $C_{25}H_{26}Sb$ [$(M - BF_4)^+$] 447.1073, found 447.1089. Anal. Calcd for $C_{25}H_{26}BF_4Sb$: C, 56.12; H, 4.90. Found: C, 56.30; H, 4.94.

Synthesis of (2-Methyl-1-propenyl)triethylammonium Tetrafluoroborate (8). To a stirred solution of the iodonium salt **4** (35 mg, 0.1 mmol) in dichloromethane (1 mL) was added triethylamine (25 mg, 0.25 mmol) under nitrogen at room temperature, and the mixture was stirred for 30 min. The organic solvent was evaporated off in vacuo to give an oil, which was washed several times with hexane by decantation. Yield of the ammonium salt **8**[3] was determined by ^1H NMR (56%).

Reaction of (Diphenylethenyl)iodonium Salt 10 with Triphenylarsine. (A) In the Presence of Diisopropylethylamine. To a stirred solution of the iodonium salt **10** (140 mg, 0.30 mmol) and triphenylarsine (184 mg, 0.60 mmol) in dichloromethane (25 mL) was added dropwise diisopropylethylamine (47 mg, 0.36 mmol) under nitrogen at 0 °C, and the mixture was stirred for 1 h at 0 °C and for 30 min at room temperature. After addition of water, the mixture was extracted with dichloromethane. Filtration and concentration under aspirator vacuum gave an oil, which was purified by preparative TLC (hexane) to give diphenylacetylene (**12**) (56 mg, 100%) and triphenylarsine (172 mg, 94%).

(B) In the Absence of a Base. A solution of the iodonium salt **10** (47 mg, 0.1 mmol) and triphenylarsine (306 mg, 1 mmol) in acetonitrile (1 mL) was heated at 50 °C for 6 h under nitrogen. Concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation to give (2,2-diphenylethenyl)triphenylarsonium tetrafluoroborate (**13**) (38 mg, 66%), contaminated with a small amount of impurity. Preparative TLC (ethyl acetate) gave the pure salt: colorless needles; mp 221−222 °C (recrystallized from dichloromethane−diethyl ether−hexane); IR (KBr) 1619, 1060 (br), 745 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 7.86 (t, $J = 7.7$ Hz, 3H), 7.71 (t, $J = 7.7$ Hz, 6H), 7.55 (t, $J = 7.7$ Hz, 1H), 7.48 (d, $J = 7.7$ Hz, 6H), 7.37 (br t, $J = 7.7$ Hz, 2H), 7.36 (br t, $J = 7.7$ Hz, 1H), 7.28 (s, 1H), 7.25 (t, $J = 7.7$ Hz, 2H), 7.11 (d, $J = 7.7$ Hz, 2H), 7.07 (d, $J = 7.7$ Hz, 2H); HRMS (FAB) calcd for $C_{32}H_{26}As$ [$(M - BF_4)^+$] 485.1250, found 485.1222. Anal. Calcd for $C_{32}H_{26}AsBF_4{\cdot}{}^1/_4H_2O$: C, 66.63; H, 4.54. Found: C, 66.56; H, 4.56.

General Procedure for Synthesis of Group 16 Alkenyl(diphenyl)onium Tetrafluoroborates 6 and 7 (Table 2). To a stirred solution of an alkenyl(phenyl)iodonium tetrafluoroborate (0.1 mmol) and a group 16 heteroatom nucleophile (Ph_2X, 0.12 mmol) in dichloromethane (1 mL) was added dropwise diisopropylethylamine (16 mg, 0.12 mmol) under nitrogen at room temperature, and the mixture was stirred for 15 min. After addition of water, the mixture was extracted with dichloromethane. Filtration and concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation to give the group 16 onium salt. Further purification of the onium salt was accomplished by recrystallization.

Diphenyl(2-methyl-1-propenyl)sulfonium tetrafluoroborate (6g): colorless needles; mp 206−207 °C (recrystallized from dichloromethane−diethyl ether−hexane); IR (KBr) 1621, 1060 (br), 747 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.00−7.81 (m, 4H), 7.78−7.57 (m, 6H), 6.77 (br s, 1H), 2.27 (br s, 3H), 2.24 (d, $J = 1.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 134.0, 131.5, 129.8, 127.5, 107.5, 26.4, 21.8; HRMS

(FAB) calcd for $C_{16}H_{17}S$ [(M − BF_4)$^+$] 241.1051, found 241.1058. Anal. Calcd for $C_{16}H_{17}BF_4S \cdot 1/2H_2O$: C, 56.99; H, 5.08. Found: C, 57.29; H, 5.18.

Diphenyl(2-methyl-1-propenyl)selenonium tetrafluoroborate (6h): colorless needles; mp 180−184 °C(recrystallized from dichloromethane−diethyl ether−hexane); IR (KBr) 1620, 1060 (br), 743 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.85−7.51 (m, 10H), 6.43 (br s, 1H), 2.21 (br s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 133.2, 131.5, 130.2, 128.2, 110.5, 26.2, 23.2; HRMS (FAB) calcd for $C_{16}H_{17}Se$ [(M − BF_4)$^+$] 287.0503, found 287.0534. Anal. Calcd for $C_{16}H_{17}BF_4Se$: C, 51.24; H, 4.57. Found: C, 51.16; H, 4.55.

Diphenyl(2-methyl-1-propenyl)telluronium tetrafluoroborate (6i): colorless plates; mp 94−96 °C (recrystallized from dichloromethane−diethyl ether−hexane, lit.[12b] mp 92−93 °C); IR (KBr) 1614, 1573, 1060 (br), 785, 736 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.70 (br d, J = 7.6 Hz, 4H), 7.63−7.45 (m, 6H), 6.28 (br s, 1H), 2.20 (d, J = 1.0 Hz, 3H), 2.17 (s, 3H); HRMS (FAB) calcd for $C_{16}H_{17}Te$ [(M − BF_4)$^+$] 339.0393, found 339.0377.

(Cyclohexylidenemethyl)diphenylsulfonium tetrafluoroborate (7g): colorless crystals; mp 165−166 °C (recrystallized from dichloromethane−diethyl ether−hexane); IR (KBr) 1606, 1075 (br), 747 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.97−7.79 (m, 4H), 7.74−7.52 (m, 6H), 6.70 (s, 1H), 2.70 (t, J = 5.7 Hz, 2H), 2.59 (t, J = 5.7 Hz, 2H), 1.82−1.51 (m, 6H); HRMS (FAB) calcd for $C_{19}H_{21}S$ [(M − BF_4)$^+$] 281.1274, found 281.1392. Anal. Calcd for $C_{19}H_{21}BF_4S$: C, 61.97; H, 5.75. Found: C, 61.93; H, 5.75.

(Cyclohexylidenemethyl)diphenylselenonium tetrafluoroborate (7h): pale brown powder; mp 124−126 °C; IR (KBr) 1614, 1060 (br), 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 6.8 Hz, 4H), 7.67−7.54 (m, 6H), 6.30 (s, 1H), 2.63−2.50 (m, 4H), 1.78−1.60 (m, 6H); HRMS (FAB) calcd for $C_{19}H_{21}Se$ [(M − BF_4)$^+$] 329.0808, found 329.0820. Anal. Calcd for $C_{19}H_{21}BF_4Se$: C, 54.97; H, 5.10. Found: C, 54.82; H, 5.05.

(Cyclohexylidenemethyl)diphenyltelluronium tetrafluoroborate (7i): colorless oil; IR (film) 1607, 1060 (br), 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.3 Hz, 4H), 7.62−7.50 (m, 6H), 6.18 (s, 1H), 2.56−2.45 (m, 4H), 1.77−1.56 (m, 6H); HRMS (FAB) Calcd for $C_{19}H_{21}Te$ [(M − BF_4)$^+$] 379.0706, found 379.0781. Anal. Calcd for $C_{19}H_{21}BF_4Te \cdot {}^1/_2H_2O$: C, 48.27; H, 4.48. Found: C, 48.65; H, 4.58.

Ligand Exchange of Alkenyl(triphenyl)onium Tetrafluoroborates 6b−d with Enolate Anion. To a stirred solution of potassium *tert*-butoxide (12 mg, 0.11 mmol) in THF (1 mL) was added a solution of 2-phenyl-1,3-indandione (24 mg, 0.11 mmol) in THF (1 mL) under nitrogen at room temperature, and the mixture was stirred for 1 h. A solution of an alkenyl(triphenyl)onium tetrafluoroborate **6b−d** (0.1 mmol) in dichloromethane (1 mL) was added, and the mixture was stirred for 5−35 min at room temperature. After addition of water, the mixture was extracted with dichloromethane. Filtration and concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation to give the group 16 onium enolate.

Phosphonium enolate 16b: 81%; reddish needles; mp 162−164 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1604, 1538, 1108, 769 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.69 (dt, $^5J_{PH}$ = 2.1 Hz, $^3J_{HH}$ = 7.5 Hz, 3H), 7.56 (dt, $^4J_{PH}$ = 3.4 Hz, $^3J_{HH}$ = 7.5 Hz, 6H), 7.40 (dd, $^3J_{PH}$ = 13.4 Hz, $^3J_{HH}$ = 7.5 Hz, 6H), 7.31−7.22 (m, 2H), 7.19−7.11 (m, 2H), 7.10 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 6.79 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.02 (d, $^2J_{PH}$ = 22.9 Hz, 1H), 2.23 (s, 3H), 1.53 (d, $^4J_{PH}$ = 2.2 Hz, 3H); HRMS (FAB) calcd for $C_{22}H_{22}P$ [(M − $C_{15}H_9O_2$)$^+$] 317.1459, found 317.1474. Anal. Calcd for $C_{37}H_{31}O_2P \cdot H_2O$: C, 79.84; H, 5.61. Found: C, 79.63; H, 5.83.

Arsonium enolate 16c: 84%; reddish needles; mp 190−193 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1603, 1539, 1497 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 7.7 Hz, 2H), 7.67 (t, J = 7.3 Hz, 3H), 7.57 (t, J = 7.3 Hz, 6H), 7.43 (d, J = 7.3 Hz, 6H), 7.25−7.20 (m, 2H), 7.18−7.12 (m, 2H), 7.09 (t, J = 7.7 Hz, 2H), 6.78 (t, J = 7.7 Hz, 1H), 6.02 (s, 1H), 2.20 (s, 3H), 1.62 (s, 3H); HRMS (FAB) calcd for $C_{22}H_{22}As$ [(M − $C_{15}H_9O_2$)$^+$] 361.0937, found 361.0936. Anal. Calcd for $C_{37}H_{31}O_2As$: C, 76.28; H, 5.36. Found: C, 76.07; H, 5.30.

Stibonium enolate 16d: 100%; reddish plates; mp 145−149 °C (recrystallized from dichloromethane−benzene); IR (KBr) 1606, 1591, 1520, 759, 739, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (br d, J = 7.5 Hz, 2H), 7.69 (d, J = 7.3 Hz, 6H), 7.53 (t, J = 7.3 Hz, 3H), 7.45 (t, J = 7.3 Hz, 6H), 6.97 (t, J = 7.5 Hz, 2H), 6.98−6.92 (m, 2H), 6.85 (t, J = 7.5 Hz, 1H), 6.72−6.66 (m, 2H), 6.10 (s, 1H), 1.89 (s, 3H), 1.58 (s, 3H); HRMS (FAB) calcd for $C_{22}H_{22}Sb$ [(M − $C_{15}H_9O_2$)$^+$] 407.0760, found 407.0777. Anal. Calcd for $C_{37}H_{31}O_2Sb$: C, 70.61; H, 4.96. Found: C, 70.28; H, 4.93.

Allylation of 2-Phenyl-1,3-indandione with Alkenyl(triphenyl)arsonium Tetrafluoroborates 6c and 7c. To a stirred solution of potassium *tert*-butoxide (9 mg, 0.08 mmol) in THF (1 mL) was added a solution of 2-phenyl-1,3-indandione (17 mg, 0.08 mmol) in THF (1.4 mL) under nitrogen at room temperature, and the mixture was stirred for 1 h. A solution of alkenyl(triphenyl)arsonium tetrafluoroborate **6c** (30 mg, 0.07 mmol) in dichloromethane (0.7 mL) was added, and the mixture was refluxed for 40 h. After addition of water, the mixture was extracted with dichloromethane, and the combined organic phase was washed with water and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated to give an oil, which was purified by preparative TLC (hexanes−ethyl acetate 8:2) to give 2-(2-methyl-2-propenyl)-2-phenyl-1,3-indandione (**14**) (16 mg, 85%): colorless crystals; mp 94−95 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1744, 1709, 1639, 1591, 1247, 915, 778, 759, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.98 (m, 2H), 7.88−7.80 (m, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.5 Hz, 1H), 4.68 (s, 1H), 4.65 (s, 1H), 3.06 (s, 2H), 1.54 (s, 3H); MS *m/z* (relative intensity) 276 (M$^+$, 100), 261 (17), 221 (24), 165 (14); HRMS calcd for $C_{19}H_{16}O_2$ (M$^+$) 276.1150, found 276.1163.

2-[(1-Cyclohexenyl)methyl]-2-phenyl-1,3-indandione (15): 83%; colorless oil; IR ($CHCl_3$) 1735, 1700, 1590, 1220 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.97 (m, 2H), 7.87−7.81 (m, 2H), 7.43 (d, J = 7.4 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 5.41 (br s, 1H), 2.98 (s, 2H), 1.80−1.60 (m, 4H), 1.33−1.13 (m, 4H); MS *m/z* (relative intensity) 316 (M$^+$, 14), 222 (100), 165 (25), 95 (50), 84 (50); HRMS calcd for $C_{22}H_{20}O_2$ (M$^+$) 316.1463, found. 316.1473.

No allylation was observed in the reactions of the phosphonium **6b** and the stibonium salts **6d** with the enolate anion of 2-phenyl-1,3-indandione in refluxing dichloromethane−THF, and these reactions gave the onium enolates **16b**,**d**.

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