Electrochemical Oxidation of Triphenylphosphine in the Presence of Allylsilanes: Voltammetric Studies and Regioselective Preparation of Allyltriphenylphosphonium Salts

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Electrochemical oxidation of triphenylphosphine (1) in dichloromethane containing allylsilanes (2) in an undivided cell afforded allyltriphenylphosphonium salts (3). The addition of 1 to 2 took place exclusively at the γ-position of 2 and the reaction was extended to provide a convenient method for the synthesis of cyclic phosphonium salts (3) bearing β-*exo*-methylene. The yields of 3 depended on the cathode material: use of a lead cathode, which has a high hydrogen overpotential, gave favorable results. Based on the results of the voltammetric study, the process of formation of 3 is suggested to involve electrophilic attack of the triphenylphosphine radical cation on 2 as the key step.

Keywords electrochemical oxidation; triphenylphosphine; allylsilane; allyltriphenylphosphonium salt; cyclic voltammetry; constant-current electrolysis

Triphenylphosphine radical cation ($Ph_3P^{+\cdot}$) (**4**) generated by one-electron oxidation of triphenylphosphine (**1**) reacts with various reagents of different nucleophilicity to give the corresponding phosphonium salts.[1)] Recently we have briefly reported a simple preparation of allytriphenylphosphonium tetrafluoroborates (**3**) effected by electrochemical oxidation of **1** in the presence of allylsilanes (**2**) (Chart 1).[2)] Allylphosphonium salts **3** are valuable reagents for the preparation of conjugated dienes, polyenes, bicyclic compounds, spirocyclic compounds, *etc.*,[3)] but the syntheses of the salts have been very limited.[4)] Therefore, the extension of this simple preparation of **3** from **1** and **2** will have potential synthetic utility. In this electrochemical oxidation, however, the two reaction pathways shown in Chart 2 should be taken into consideration, because the voltammetric peak potentials of **1** and **2** are close to each other: some allylsilanes indeed have anodic potentials less positive than that of **1**. Path a is a process initiated by the oxidation of **1**, involving an electrophilic attack of **4** on **2**. Path b, on the contrary, involves initial one-electron oxidation of **2** followed by a nucleophilic attack of **1** on the radical cation $\mathbf{2}^{+\cdot}$ or some intermediate derived from $\mathbf{2}^{+\cdot}$.

In this paper, we discuss first the reaction process for the formation of **3** on the basis of the results of cyclic voltammetry of **1** and **2**, and then describe the synthesis of cyclic phosphonium salts **3** bearing β-*exo*-methylene, together with the effects of various factors on the macroscale electrolysis.

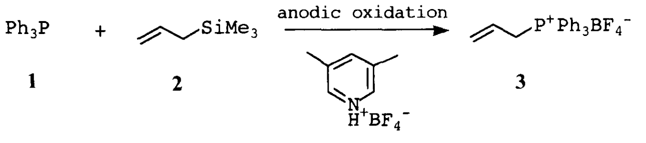
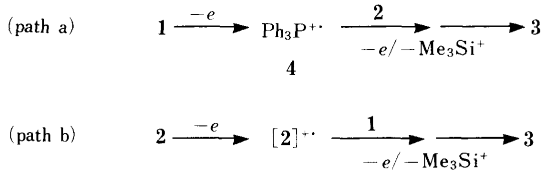


Chart 1



$$\text{(path a)}\quad 1 \xrightarrow{-e} \underset{\mathbf{4}}{Ph_3P^{+\cdot}} \xrightarrow[-e/-Me_3Si^+]{2} \longrightarrow 3$$

$$\text{(path b)}\quad 2 \xrightarrow{-e} [2]^{+\cdot} \xrightarrow[-e/-Me_3Si^+]{1} \longrightarrow 3$$

Chart 2

Results and Discussion

Cyclic voltammetry was carried out with a glassy carbon disk working electrode in acetonitrile containing 0.1 M lithium tetrafluoroborate. All potentials were measured against an Ag/AgCl reference electrode, whose potential was +0.40 V *vs.* a saturated calomel electrode (SCE). Typical voltammograms for **1**, allyltrimethylsilane (**2a**), and an equimolar mixture of the two are shown in Fig. 1. Under the experimental conditions, **1** and **2a** showed single irreversible anodic peaks at 1.40 and 1.65 V, respectively.[5)] In the case of the mixture of **1** and **2a**, the peak of **2a** unexpectedly shifted to 1.95 V, while that of **1** was essentially unchanged (Fig. 1c). Accordingly, the effect of **1** on the peak potential (E_{pa}) of **2a** was examined further. At a constant concentration of **2a** (5 mM), the E_{pa} value increased and approached a limiting value with increasing amount of **1** (Fig. 2). Similar voltammetric behavior was observed for other allylsilanes (**2**) examined (Table I). When measured independently, the E_{pa} values of four allylsilanes (**2b**, **2c**, **2f**,

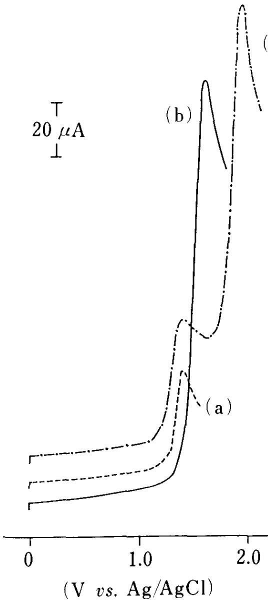


Fig. 1. Cyclic Voltammograms of **1**, **2**, and the Mixture of These Compounds in Acetonitrile Containing 0.1 M $LiBF_4$

(a) **1** (5 mM), (b) **2a** (5 mM), (c) an equimolar mixture (**1**, 5 mM; **2a**, 5 mM). Voltage sweep rate: $50\,mVs^{-1}$. The curves for the reverse sweep are omitted for simplicity.

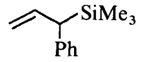
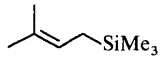
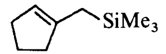
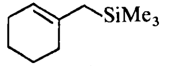
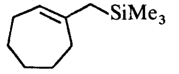
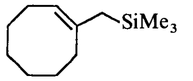
and **2g**) out of seven were smaller than that of **1** (1.40 V). In the equimolar mixture of **1** and **2**, however, the oxidation of **1** preceded without exception. These results strongly suggested that the formation of **3** proceeds *via* path a in Chart 2, involving the electrophilic attack of the radical cation **4** on the unoxidized form of **2**.

The anodic shifts of the oxidation peak of **2** in the presence of **1** can be rationalized in terms of the different adsorptivity of the substrates in the electrochemical process. Since aromatic compounds are known to be good adsorbates on an anode,[6] the phosphine **1** will be adsorbed preferentially onto the electrode to hinder the electron transfer from the other substrate (**2**). In agreement with this assumption, the E_{pa} values of **2** were not affected by an aliphatic phosphine such as tributylphosphine.

In the macroscale electrolysis, allylsilane (**2a**) was selected as a model compound, and its conversion to the allyltriphenylphosphonium salt (**3a**) was examined first. Table II summarizes the results of constant-current electrolysis (CCE) performed in an undivided cell under various conditions. Dichloromethane and 3,5-lutidinium tetrafluoroborate (3,5-LutBF$_4$) seem preferable as the solvent (runs 2—4) and the supporting electrolyte (runs 4 and 5), respectively.

It is interesting to note that the formation of **3a** is affected by the cathode material (runs 5—7). Among the cathode materials employed in the CCE, the lead plate gave the best

TABLE I. Voltammetric Peak Potentials of Allylsilanes **2** (5 mM) in Acetonitrile Containing 0.1 M LiBF$_4$: 50 mVs^{-1}

	Allylsilane (**2**)	Peak potential (E_{pa}) (V *vs.* Ag/AgCl)	
a		1.95[a]	(1.65)[b]
b		1.57[a]	(1.34)[b]
c		1.60[a]	(1.28)[b]
d		1.64[a]	(1.40)[b]
e		1.67[a]	(1.46)[b]
f		1.58[a]	(1.34)[b]
g		1.61[a]	(1.37)[b]

a) In the presence of **1** (5 mM). *b*) In the absence of **1**.

TABLE II. Results of Electrolysis of **1** in the Presence of **2a**[a]

Run	Solvent	Supporting electrolyte	Anode[b]	Cathode[c]	Yield of **3a** (%)[d]
1	CH_3CH	LiBF$_4$	GC	SS	28
2	CH_3CN	2,6-LutBF$_4$	GC	SS	31
3	THF[e]	2,6-LutBF$_4$	GC	SS	28
4	CH_2Cl_2	2,6-LutBF$_4$	GC	SS	50
5	CH_2Cl_2	3,5-LutBF$_4$	GC	SS	55
6	CH_2Cl_2	3,5-LutBF$_4$	GC	Pt	23
7	CH_2Cl_2	3,5-LutBF$_4$	GC	Pb	71
8	CH_2Cl_2	3,5-LutBF$_4$	GP	Pb	65

a) A mixture of **1** (3 mmol) and **2a** (1.5 mmol) was subjected to CCE (20 mA) in an undivided electrolysis cell. Current density was 1 mA/cm^2. *b*) GC, glassy carbon plate; GP, graphite plate. *c*) SS, stainless steel plate; Pt, platinum plate; Pb, lead plate. *d*) Isolated yield based on **2a**. *e*) THF, tetrahydrofuran.

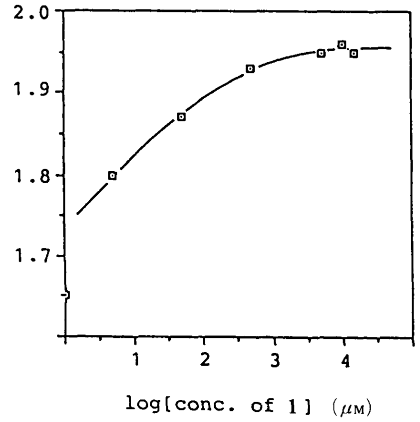


Fig. 2. Plots of the Peak Potential of **2a** *vs.* Logarithm of the Concentration of **1**

Concentration: **2a**, 5 mM; **1**, 0.005—15 mM. Conditions: solvent, acetonitrile; supporting electrolyte, LiBF$_4$ (0.1 M); voltage sweep rate, 50 mVs^{-1}.

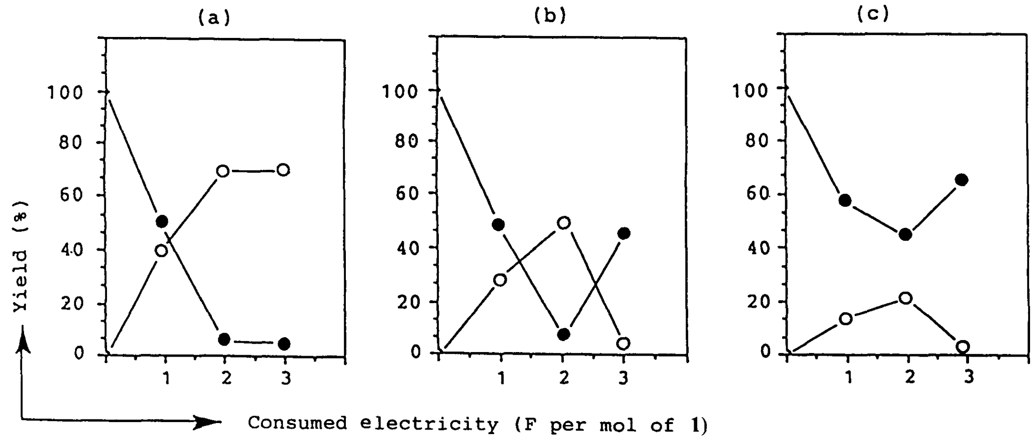
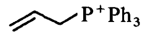
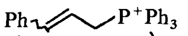
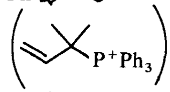
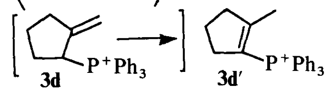
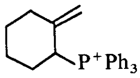
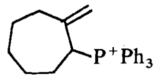
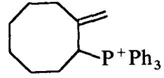


Fig. 3. Plots of the Yield of **3a** (○) and **1** Recovered (●) *vs.* Consumed Electricity in the CCE of **1** (3 mmol) in the Presence of **2a** (1.5 mmol) in CH_2Cl_2 Containing 0.2 M 3,5-LutBF$_4$

(a) with a lead plate cathode, (b) with a stainless steel plate cathode, (c) with a platinum plate cathode. The lines connecting the experimental points are shown for convenience, and have no physical significance.

TABLE III. Preparation of **3** by CCE of **1** in the Presence of **2**[a)]

2	**3**[b)]	Yield (%)[c)]
a		71
b		51
c		0
d	 **3d** **3d'**	24
e		27
f		52
g		53

a) A mixture of **1** (3 mmol) and **2** (1.5 mmol) in CH_2Cl_2 containing 0.2 M 3,5-LutBF$_4$ was subjected to CCE (20 mA) in an undivided cell with a glassy carbon-plate anode and a lead plate cathode. Current density was 1 mA/cm^2. *b*) Counter anion: BF_4^-. *c*) Isolated yield based on **2**.

yield of **3a** (run 7). The change in the yield of **3a** and the recovery of **1** during the course of CCE (Fig. 3) suggest that **3a** once produced at the anode is reduced at the cathode to regenerate **1**. Allyltriphenylphosphonium salts have been reported to give **1** on cathodic reduction.[7)] The efficiency of this reduction seems to be inversely related to the order of hydrogen overpotential of the cathode material. This prediction is supported by the observation that the voltammetric reduction peak of **3a** in acetonitrile shifted to more negative potentials with increase in the hydrogen overpotential of the cathode: −1.3, −1.5 and −1.6 V at a platinum disk, a glassy carbon disk, and a hanging mercury electrode, respectively.[8,9)] When the CCE was performed with a platinum cathode but in a divided electrolysis cell, where the reduction of the oxidation products is eliminated, the yield of **3a** increased to 72% (*cf.* Table II, run 6).

The CCE of **1** in the presence of **2b**—**g** (see, Table I) was examined under the optimal conditions found for **2a**, and the results are summarized in Table III. The products **3b** and **3e**—**g** can be added to the list of examples of **3** accessible by electrochemical preparation.[2)]

As reported in the reactions of allylsilanes with a range of electrophiles,[10)] all the products isolated are considered to be formed *via* the attack of the radical cation **4** exclusively at the γ-position of the allylic system in **2**. No regioisomer of **3** was detected in the CCE under the present conditions. The failure to obtain a stable product from **2c** can be atttibuted to the steric repulsion between the radical cation **4** and the two γ-methyl groups of **2c**. Although the isolated product in the electrolysis with **2d** was not the expected γ-adduct **3d** but the 1-alkenylphosphonium salt **3d'**, the formation of the latter can be explained in terms of a prototropic rearrangement of **3d** initially produced.

Among the products **3**, the phosphonium salts possessing an exomethylene group (**3e**—**g**) are of special interest, because these phosphonium salts have never been prepared by conventional methods.[3a,b)] In our previous report on the electrochemical preparation of 1-alkenyltriphenylphosphonium salts,[11)] as acyclic phosphonium salt of type R–CH=CH–P$^+$PH$_3$X$^-$ (A) could not be obtained in pure form from **1** and R–CH=CH$_2$, [R$\neq$H], probably because a hardly separable mixture of A and other phosphonium salts had been formed. Since allylphosphonium salts **3** are known to be converted easily to 1-alkenylphosphonium salts,[3e)] the present method, which gave **3** regioselectively, will be also useful in this connection.

Experimental

Melting points and boiling points are uncorrected. Proton and carbon-13 nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectra were recorded on a JEOL JNM-PMX60SI (60 MHz) or a JEOL JNM-GX400 (400 MHz) spectrometer. Chemical shifts were measured relative to tetramethylsilane. ^{13}C-NMR spectra were obtained by the DEPT (distortionless enhancement by polarization transfer) method.[12)] Infrared (IR) spectra were recorded on a JASCO IRA-1 spectrophotometer. Low- and high-resolution mass spectra (MS) were recorded on a JEOL JMS-D300 instrument.

Materials 3,5-LutBF$_4$ and 2,6-LutBF$_4$ were prepared as described previously[13)] and stored over silica gel under reduced pressure (1 mmHg) at 35 °C. Acetonitrile was distilled over P_2O_5 and stored under a nitrogen atmosphere. Dichloromethane was distilled over P_2O_5 and stored over molecular sieves. Allylsilane **2a** was obtained commercially and used without further purification. Allysilanes **2b**,[14)] **2c**,[15)] **2d**,[16)] and **2e**[16)] were prepared by the reported methods. Other chemicals were commercial products and were purified either by distillation or by recrystallization.

Preparation of Allylsilanes 2f and 2g A procedure similar to that reported by Kumada *et al.*[16)] was employed. Anhydrous nickel acetylacetonate (1.4 g, *ca.* 5 mmol) was placed in a 300 ml round-bottomed flask, then a 1.1 M solution of trimethylsilylmethylmagnesium chloride in ether (164 ml) and (cyclohepten-1-yl)diethylphosphate (22.4 g, 90 mmol)[17)] or (cycloocten-1-yl)diethylphosphate (23.6 g, 90 mmol)[17)] were added successively. The mixture was stirred at ambient temperature under a nitrogen atmosphere for 50 h, and then hydrolyzed with 5% HCl (250 ml) at 0 °C. The resulting mixture was extracted with ether (3 × 100 ml). The ether phase was washed successively with 10% NaHCO$_3$ (200 ml) and water (200 ml). After evaporation of the ether, allylsilane **2f** (12.0 g, 73%) or **2g** (13.1 g, 74%) was distilled under a reduced pressure.

(Cyclohepten-1-yl-methyl)trimethylsilane (**2f**): bp 73—75 °C (11 mmHg). ^{1}H-NMR (CCl$_4$) δ: 0.02 (9H, s), 1.1—1.8 (8H, m), 1.9—2.3 (4H, m), 5.27 (1H, m). Exact mass Calcd for $C_{11}H_{22}Si$: 182.1491. Found: 182.1506.

(Cycloocten-1-yl-methyl)trimethylsilane (**2g**): bp 78—81 °C (11 mmHg). ^{1}H-NMR (CCl$_4$) δ: 0.03 (9H, s), 1.1—1.8 (10H, m), 1.9—2.3 (4H, m), 5.13 (1H, m). Exact mass Calcd for $C_{12}H_{24}Si$: 196.1647. Found: 196.1695.

Cyclic Voltammetry Cyclic voltammetry was carried out at 25 °C using a Hokuto Denko HR-101B dual potentiostat/galvanostat with a Hokuto Denko HB-104 function generator. Voltammograms were recorded on a Yokogawa Electric Works type 3086 X-Y recorder. A glassy carbon disk working electrode was prepared as described previously.[18)] The counter electrode was a platinum plate (0.7 × 1.5 cm). The reference electrode was an Ag wire (1 mm diameter) coated with AgCl, which was prepared by the reported method.[19)]

Preparative Scale Electrolysis Preparative scale electrolysis was carried out with a Hokuto Denko HA-301 or a HA-104 potentiostat/galvanostat in conjunction with a Hokuto Denko HF-201 coulomb/ampere-hour meter. A 50 ml sample tube of 3.5 cm diameter and 7.5 cm height was employed as the undivided electrolysis cell. The cell was equipped with a glassy carbon plate (2 × 4 cm) and a lead plate cathode (0.4 × 4 cm) through a silicon stopper.

Preparation of 3. General Procedure A solution of **1** (3 mmol) and **2** (1.5 mmol) in anhydrous dichloromethane (40 ml) containing 0.2 M 3,5-LutBF$_4$ was subjected to constant current electrolysis (20 mA; current density, 1 mA/cm^2) at ambient temperature under a nitrogen atmosphere until 2 F per mol of **1** had been consumed. The electrolyzed solution was concentrated *in vacuo*. Water (100 ml) was added to the residue and the mixture was extracted with chloroform (3 × 50 ml). The combined organic layer was dried over MgSO$_4$, condensed to *ca.* 5 ml under a reduced pressure and then added dropwise to ether (50 ml). The crystallized phosphonium salt **3** was purified by passage through a short column of silica gel with ethyl acetate as a eluent. Analytical samples were further recrystallized from CH$_2$Cl$_2$–ether. Essentially the same procedure was applied to the electrolysis in a divided cell, whose anode compartment was separated by a sintered glass disk from the cathode.

Allyltriphenylphosphonium Tetrafluoroborate (**3a**): mp 161—162 °C. IR ($CHCl_3$): 1630, 1590, 1080 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.5—7.9 (15H, m, Ph_3P), 5.3—5.7 (3H, m, $\underline{H}_2C=C\underline{H}$–), 4.2 (2H, dd, $J=15$, 6 Hz, $\underline{H}_2C$–P^+). *Anal.* Calcd for $C_{21}H_{20}BF_4P$: C, 64.65; H, 5.17. Found: C, 64.68; H, 5.01.

(3-Phenyl-2-penten-1-yl)triphenylphosphonium Tetrafluoroborate (**3b**): mp 178—180 °C. IR (KBr): 1620, 1590, 1080 cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 7.9—7.7 (15H, m, Ph_3P), 7.29 (5H, br s, Ph), 6.60 (1H, br d, $J=15.7$ Hz, $PhC\underline{H}=CH$), 6.1—6.0 (1H, m, $PhCH=C\underline{H}$), 4.24 (2H, dd, $J=15.8$, 7.6 Hz, $\underline{H}_2C$–P^+). *Anal.* Calcd for $C_{27}H_{24}BF_4P$: C, 69.55; H, 5.19. Found: C, 69.61; H, 5.12.

(2-Methyl-1-cyclopenten-1-yl)triphenylphosphonium Tetrafluoroborate (**3d′**): mp 134—136 °C. IR ($CHCl_3$): 1600, 1585, 1080 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.9—7.7 (m, 15H), 2.8—1.3 (m, 9H). *Anal.* Calcd for $C_{24}H_{24}BF_4P$: C, 67.00; H, 5.62. Found: C, 66.98; H, 5.66.

(2-Methylene-1-cyclohexyl)triphenylphosphonium Tetrafluoroborate (**3e**): mp 187—189 °C. IR (KBr): 1640, 1585, 1080 cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 7.9—7.6 (15H, m, Ph_3P), 5.07 (1H, br s, *cis-* or *trans-*H of *exo*-methylene), 4.58 (1H, br s, *cis-* or *trans-*H of *exo*-methylene), 4.4—4.3 (1H, m, $\underline{H}C$–P^+), 2.4—1.4 (8H, m). ^{13}C-NMR (CD_3CN) δ: 115.9 ($J_{PC}=8.4$ Hz, $H_2\underline{C}=C$), 96.7 (C(2)), 39.7 ($J_{PC}=48.1$ Hz, C(1)), 135.6 (*p*-C of Ph_3P), 135.2 (*o*-C), 131.2 (*m*-C), 119.1 ($J_{PC}=83.9$ Ha, $\underline{C}$–P^+ of Ph), 37.4, 29.2, 28.0, 26.0. *Anal.* Calcd for $C_{25}H_{26}BF_4P$: C, 67,59; H, 5.90. Found: C, 67.50; H, 5.98.

(2-Methylene-1-cycloheptyl)triphenylphosphonium Tetrafluoroborate (**3f**): mp 200—202 °C. IR (KBr): 1625, 1585, 1080 cm^{-1}. ^{1}H-MMR (CD_3CN) δ: 7.9—7.7 (15H, m, Ph_3P), 5.25 (1H, br s, *cis-* or *trans-*H of *exo*-methylene), 5.02 (1H, br s, *cis-* or *trans-*H of *exo*-methylene), 4.7—4.6 (1H, m, $\underline{H}C$–P^+), 2.4—1.0 (10H, m), ^{13}C-NMR (CD_3CN) δ: 123.3 ($J_{PC}=9.9$ Hz, $H_2\underline{C}=C$), 96.6 (C(2)), 40.9 ($J_{PC}=43.5$ Hz, C(1)), 135.9 (*p*-C of Ph_3P), 135.2 (*o*-O), 131.2 (*m*-C), 118.8 ($J_{PC}=82.4$ Hz, $\underline{C}$-P^+ of Ph), 35.4, 32.1, 29.8, 28.6, 27.3. *Anal.* Calcd for $C_{26}H_{28}BF_4P$: C, 68.14; H, 6.16. Found: C, 67.96; H, 6.17.

(2-Methylene-1-cyclooctyl)triphenylphosphonium Tetrafluoroborate (**3g**): mp 179—181 °C. IR (KBr): 1620, 1590, 1080 cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 7.9—7.7 (15H, m, Ph_3P), 4.01 (1H, br s, *cis-* or *trans-*H of *exo*-methylene), 3.97 (1H, br s, *cis-* or *trans-*H of *exo*-methylene), 3.3—3.1 (1H, m, $\underline{H}C$–P^+Ph_3), 2.2—1.4 (12H, m). ^{13}C-NMR (CD_3CN) δ: 122.3 ($J_{PC}=8.3$ Hz, $H_2\underline{C}=C$), 95.4 (C(2)), 33.4 ($J_{PC}=47.6$ Hz, C(1)), 136.1 (*p*-C of Ph_3P), 135.1 (*o*-C), 131.2 (*m*-C), 119.3 ($J_{PC}=85.5$ Hz, $\underline{C}$–P^+ of Ph), 30.9, 30.2, 28.4, 27.6, 27.3, 26.6. *Anal.* Calcd for $C_{27}H_{30}BF_4P$: C, 68.66; H, 6.40. Found; C, 68.64; H, 6.48.

References and Notes

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