Reaction of Olefins with Dimethyl(methylthio)sulfonium Salts in the Presence of Triphenylphosphine. Preparation of Vinylphosphonium Salts

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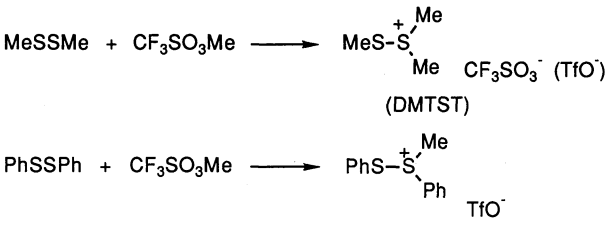
Olefins were effectively converted into the corresponding (2-methylthioalkyl)triphenylphosphonium salts by the reaction with dimethyl(methylthio)sulfonium salts in the presence of triphenylphosphine. 2-Triphenylphosphonioalkyldimethylsulfonium salts, synthesized by alkylation of the corresponding methylthiophosphonium salts, react with 1,8-diazabicyclo[5.4.0]undec-7-ene or aq NaOH to afford the corresponding vinylphosphonium salts or vinylphosphine oxides in good yields.

Dimethyl(methylthio)sulfonium tetrafluoroborate (DMTSF) is widely used for the synthesis of heterocycles and unsaturated thioacetals.[1] However, there is no report on the reaction of DMTSF with an olefin and triphenylphosphine. Recently, we have communicated a convenient synthesis of 2-methylthioalkylphosphonium salts (**1**) by the reaction of DMTSF with olefins and triphenylphosphine.[2] Now, we would like to report the full details of the syntheses of 2-methylthioalkyltriphenylphosphonium salts **1**, phosphoniosulfonium salts (**2**), and vinyltriphenylphosphonium salts (**3**).

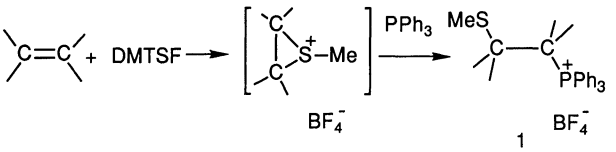
Results and Discussion

Preparation of Dimethyl(methylthio)sulfonium Trifluoromethanesulfonate (Triflate) and Dimethyl(phenylthio)sulfonium Triflate. Dimethyl(methylthio)sulfonium trinitrobenzenesulfonate was originally prepared by Helmkamp and co-worker. However, there are few reports regarding this salt.[3] In 1965, Meerwein and coworkers reported the preparation of DMTSF by the reaction of dimethyl disulfide with trimethyloxonium tetrafluoroborate.[4] Smallcome and Caserio carried out the kinetic study of this compound with dimethyl disulfide or azasulfenylation of alkenes by using of this salt.[5] Trost and co-workers applied this salt to the synthesis of macrocyclic compounds.[6] We also synthesized dimethyl(methylthio)sulfonium triflate (DMTST) by the reaction of dimethyl disulfide with methyl triflate in dichloromethane as colorless crystals in 84% yield. Its ^{1}H NMR spectrum (CD_3NO_2) shows signals at δ=2.93 (methylthio) and 3.25 (methyl) ppm in accordance with the reported values.[7] However, its melting point (53—55°C) is higher than the reported one (28—36°C).[7] Although DMTST is stable at room temperature in dichloromethane, combustion analysis does not give satisfactory result because of very hygroscopic nature. When a similar reaction was carried out by using diphenyl disulfide instead of dimethyl disulfide, the corresponding phenylthiosulfonium triflate was obtained (Scheme 1). Compared with DMTST, this salt is too labile to be isolated.

Preparation of 2-Methylthioalkylphosphonium Salts 1. We first tried the reaction of cyclohexene with DMTSF. Treatment of cyclohexene with DMTSF resulted in the formation of 1,2-episulfonium tetrafluoroborate which reacted with triphenylphosphine to give the corresponding 2-methylthiocyclohexyltriphenylphosphonium tetrafluoroborate (**1b**) in 88% yield. Other reactions were also carried out in a similar manner (Scheme 2, Table 1).



Scheme 1.

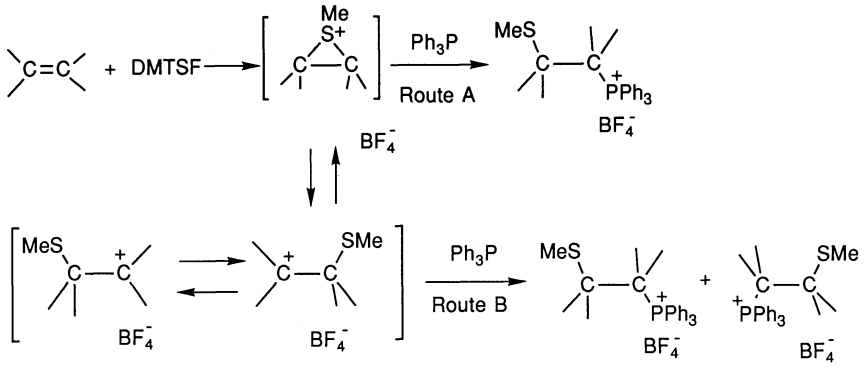


Scheme 2.

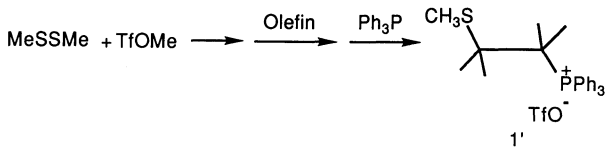
Table 1. Preparation of 2-Methylthioalkylphosphonium Salts (**1**) Using of DMTSF

Olefin	Salts	Yield / %	Mp / °C
Cyclopentene	**1a**	86	126—127
Cyclohexene	**1b**	88	223—224
Styrene	**1c**	90	198—199
1-Heptene	**1d**	93	118—119
α-Methylstyrene	**1e**	82	131—132
Allyl alcohol	**1f**	38	240—241[a]

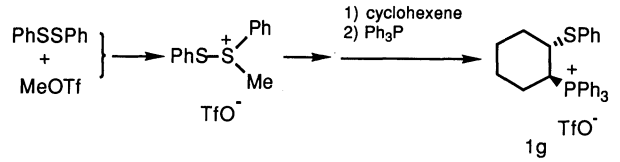
a) Mp of BPh_4 salts.



Mechanism.



Scheme 3.



Scheme 4.

Table 2. Preparation of 2-Methylthioalkylphosphonium Salts Using of DMTST

Olefin	Salts	Yield %	Mp °C
Cyclopentene	**1a'**	88	230—231[a]
Cyclohexene	**1b'**	87	191—192
Styrene	**1c'**	93	170—171
1-Heptene	**1d'**	95	258—259[a]

a) Mp of BPh_4 salts.

The reaction is not only regioselective but also stereoselective. The stereochemistry of the addition is *trans*, as has been shown for cyclopentene and cyclohexene. As to the formation of the the phosphonium salts **1**, the following two mechanisms are possible. Treatment of olefin with DMTSF forms the corresponding episulfonium ion, which directly react with triphenylphosphine to give **1** (Route A). In the other case, the episulfonium ion may be transformed to a carbocation which results in the formation of **1** on reaction with triphenylphosphine (Route B).

The trans stereoselectivity observed with cyclohexene and cyclopentene and the regioselectivity observed with 1-heptene and allyl alcohol, in which triphenylphosphine adds to the less hindered methylene carbon, suggests that the reaction would proceed in an S_N2 mechanism fashion via the episulfonium intermediate (Route A). On the other hand, the regioselectivity in the reaction of styrene or 1-methylstyrene suggests that the reaction proceeded via the carbocation intermediate (Route B).

By using DMTST, similar reactions were carried out. Generally, yields of the salts were improved. Additionally, the reaction can be carried out without isolation of DMTST (Scheme 3).

Olefins carrying a functional group such as acrylonitrile or α,β-unsaturated carbonyl compounds failed to give the corresponding phosphonium salts due to their electron deficient nature. The reaction of methylphenyl(phenylthio)sulfonium triflate with cyclohexene and triphenylphosphine was also carried out. The corresponding phosphonium triflate [**1g**] was obtained in 27% yield (Scheme 4).

Since methylphenyl(phenylthio)sulfonium triflate is less reactive and less stable than DMTST, reactions with other olefins were unsuccesful.

Preparation of Phosphoniosulfonium Salts 2. Methylation or ethylation using Meerwein reagents is a popular method for the preparation of onium salts.[8] We applied this method to the synthesis of phosphoniosulfonium salts. The reaction of (2-methylthioalkyl)triphenylphosphonium salts with trimethyloxonium tetrafluoroborate afforded the corresponding phosphoniosulfonium salts in good yields (Scheme 5).

Reaction of Phosphoniosulfonium Salts 2. It is well known that the reaction of sulfonium salts with bases affords the corresponding ylides, which react with carbonyl compounds to give epoxides in good yields.[9] Since phosphoniosulfonium salts **2** form a new class of compounds whose reactivities are unknown and of

interest, we then tried the reaction of these salts with bases. Treatment of **2a** with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in refluxing dichloromethane resulted in the formation of 1-cyclopentenyltriphenylphosphonium tetrafluoroborate (**3a**) in 76% yield. Salt **2a** easily eliminates dimethyl sulfide to give the corresponding **3a**.

Synthesis of Triphenylvinylphosphonium Salts from (Methylthio)triphenylphosphonium Salts. In recent years, a number of research groups have demonstrated the usefulness of vinylphosphonium salts in the synthesis of a wide variety of acyclic, polycyclic, and heterocyclic compounds.[10] For example, Minami and co-workers reported that the reaction of (1-cyclobutenyl)triphenylphosphonium perchlorate with the sodium salt of salicylaldehyde afforded 2,2a-dihydro-1*H*-cyclobuta[*b*]chromene in 47% yield. The method involves the addition of triphenylphosphine to allyl bromide by base-catalyzed prototropic rearrangement, addition to alkynylphosphonium salts, oxidative elimination of phenyl selenoxide from cyclic alkyl phenyl selenides, and Pd-catalyzed vinylation of triphenylphosphine with vinyl triflates.[11] Vedejs et al. reported the synthesis of cyclopentenyltriphenylphosphonium tetrafluoroborate by the dehydration of the corresponding hydroxycycloheptylphosphonium salts.[12]

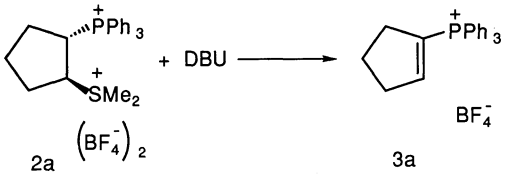
We then tried the syntesis of vinylphosphonium salts from salts **1**. Treatment of (2-methylthiocyclohexyl)triphenylphosphonium salts (**1b′**) with DBU afforded the corresponding vinylphosphonium salts in 94% yield (Scheme 7, Table 5).

However, when **1c′** was used as a substrate, starting **1c′** was recovered almost quantitatively. Because α-hydrogen abstraction by DBU does not occur.

Preparation of Vinylphosphine Oxides. Many workers have reported the synthesis of phosphine oxide from the corresponding phosphonium salts.[10,13] We also tried the reaction of 2-methylthiophosphonium salts with aq sodium hydroxide to obtain the corresponding phosphine oxides. However, the observed products were vinyl phosphine oxides.(Scheme 8, Table 6)

However, triphenylphosphine oxide was obtained in 75% yield by the reaction of **1c** with aq NaOH. Since the α-carbon in **1c** is sterically crowded, hydroxide anion might attack the phosphorus atom but not the α-hydrogen.

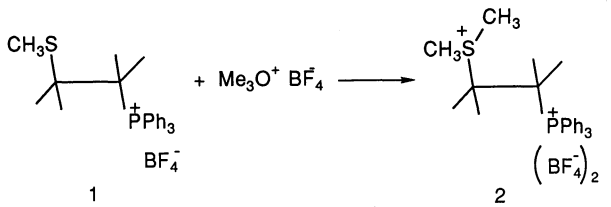
In summary, the reaction of DMTST (or DMTSF) with olefins followed by the addition of triphenylphosphine afforded the corresponding 2-methylthioalkylphosphonium salts, which were further treated with bases to give the corresponding vinylphosphonium salts or vinyl phosphine oxides. This new method provides a



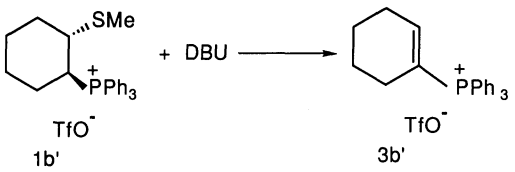
Scheme 6.

Table 4. Preparation of vinylphosphonium Salts from Phosphoniosulfonium Salts

Salt	Product	Yield %	Mp °C
Cyclopentyl	**3a**	79	245—246
Cyclohexyl	**3b**	76	223—224



Scheme 5.



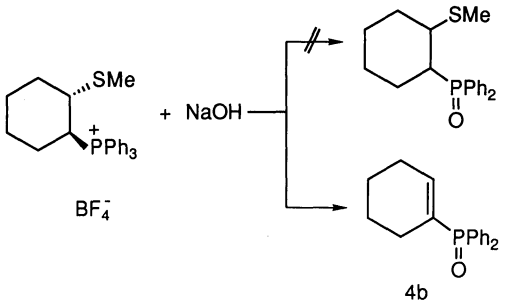
Scheme 7.

Table 3. Preparation of Phosphoniosulfonium Salts

Salt	Phosphoniosulfonium salt	Yield %	Mp °C
Cyclopentyl	**2a**	70	226—227
Cyclohexyl	**2b**	76	215—216

Table 5. Preparation of Vinylphosphonium Salts

Thiomethylphosphonium salt	Vinylphosphonium salt	Yield %
Cyclopentyl	**3a′**	95
Cyclohexyl	**3b′**	94



Scheme 8.

Table 6. Preparation of Vinyl Phosphine Oxides

Substrate	Product		Yield
			%
Cyclopentyl	**4a**	Cyclopentenyl	92
Cyclohexyl	**4b**	Cyclohexenyl	94

general two step synthesis of vinylphosphonium salts starting from easily available olefins.

Experimental

General. All reactions were conducted under a positive atmosphere of dry nitrogen. Diethyl ether and tetrahydrofuran were distilled from sodium diphenylketyl. Flash chromatography was performed on Merck 70—230 mesh silica gel. Melting points are uncorrected. ^{1}H NMR spectra were determined with a JEOL FX-90Q or a GX-400 spectrometer.

Preparation of Dimethyl(methylthio)sulfonium Triflate (DMTST). To a solution of methyl triflate (6.22 mL, 0.06 mol) in dichloromethane (50 mL) was added a solution of dimethyl disulfide (4.7 g, 0.05 mol) in dichloromethane (20 mL) under a nitrogen atmosphere at 0°C. After stirring for 3 h, 40 mL of ether was added to this solution. Colorlss crystals precipitated were filtered under a nitrogen atmosphere to give colorless crystals of DMTST (10.8 g, 0.042 ml, 84%): Mp 53—55°C (lit,[7] 28—36°C). ^{13}C NMR (CD_3NO_2) δ=17.8 (SMe), 32.0 (Me).

Preparation of 2-Methylthiocyclopentyltriphenylphosphonium Tetrafluoroborate (1a). To a solution of DMTSF (4.0 g, 20 mmol) in 50 mL of dichloromethane was added a solution of cyclopentene (1.39 g, 20 mmol) in dichloromethane (10 mL) at room temperature. After stirring for 30 min, a solution of triphenylphosphine (5.35 g, 20 mmol) in dichloromethane (20 mL) was added to this solution. After stirring for additional 15 h, the reaction mixture was filtered and evaporated to afford pale yellow crystals, which were washed with ether and recrystallized from methanol to give colorless crystals of **1a**.(8.0 g, 17.2 mmol, 86%) Mp. 126—127°C. ^{1}H NMR ($CDCl_3$) δ=1.43—1.50 (m, 1H, C-3 methylene), 1.51—1.58 (m, 1H, C-4 methylene), 1.74—1.81 (m, 1H, C-5 methylene), 1.83—1.90 (m, 1H, C-3 methylene), 1.90—1.96 (m, 1H, C-4 methylene), 2.24 (s, 3H, SMe), 2.56—2.66 (m, 1H, C-5 methylene), 3.12—3.20 (m, 1H, S-CH), 3.75—3.84 (m, 1H, P-CH), 7.52—7.85 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=15.1 (SMe), 24.4 (C-4), 28.9 (d, C-5), 33.8 (d, C-3), 37.2 (d, C-1), 47.3 (C-2), 117.4—135.6 (Ar). Found: C, 61.73; H, 5.80%. Calcd for $C_{24}H_{26}BF_4PS$: C, 62.08; H, 5.66%. Other phosphonium salts **1b—h** were prepared in a similar manner. 2-Methylthiocyclohexyltriphenylphosphonium fluoroborate (**1b**): Mp 223—224°C. ^{1}H NMR ($CDCl_3$) δ=1.22—1.36 (m, 1H, C-4 methylene), 1.42—1.48 (m, 1H, C-6 methylene), 1.64 (s, 3H, SMe), 1.80—2.09 (m, 7H, C-2 methine, C-3,4, and 5 methylene), 2.17—2.21 (m, 1H, C-6 methylene), 4.15—4.24 (m, 1H, C-1 methine), 7.59—7.77 (m Ar), 7.79—7.97 (m, Ar). ^{13}C NMR ($CDCl_3$) δ=14.0 (C-7), 24.8 (d, C-5), 25.8 (C-4), 29.7 (C-6), 33.8 (C-3), 36.3 (d, C-1), 46.3 (C-2), 119.0-134.2 (Ar). Found: C, 62.88; H, 60.9%. Calcd for $C_{25}H_{28}BF_4PS$: C, 62.77; H, 5.91%.

1c: Mp 198—199°C; ^{1}H NMR ($CDCl_3$) δ=2.07 (s, 3H, Me), 3.27 (m, 2H, CH_2), 5.05 (m, 1H, CH), 7.06—7.75 (m, 20H, Ph). Found: C; 64.70; H, 5.13%. Calcd for $C_{27}H_{26}BF_4PS$: C, 64.81; H, 5.25%.

1d: Mp 118—119°C; ^{1}H NMR ($CDCl_3$) δ=0.74—3.79 (m, 14H, heptyl), 1.83 (s, 3H, SMe), 7.72—7.83 (m, 15H, Ph). Found: C; 63.06; H, 6.35%. Calcd for $C_{26}H_{31}BF_4PS$: C, 62.39; H, 6.35%.

1e: Mp 131—132°C; ^{1}H NMR ($CDCl_3$) δ=2.19 (s, 3H, SMe), 2.28 (s, 3H, Me), 2.52 (s, 2H, CH2), 7.65—8.69 (m, 20H, Ar). ^{13}C NMR ($CDCl_3$) δ=17.6 (SMe), 21.6 (Me), 26.2 (d, P-C), 42.3 (CH_2), 115.3—135.38 (Ar). Found: C, 65.41; H, 5.55%. Calcd for $C_{28}H_{26}BF_4PS$: C, 65.38; H, 5.50%.

1f: Mp 240—241°C; ^{1}H NMR (CD_3SOCD_3) δ=1.81 (s, 3H, SMe), 2.54—2.79 (m, 1H, CH), 3.16—4.11 (m, 2H, P-CH_2), 5.06—5.28 (m, 2H, CH_2), 6.85—7.70 (BPh_4), 7.74—7.82 (15H, Ph). ^{13}C NMR ($CDCl_3$) δ=13.8 (SMe), 24.4 (d, CH), 42.7 (d, CH_2), 64.2 (d, P-CH_2), 121.5—135.7 (Ar). Found: C, 80.86; H, 6.86%. Calcd for $C_{46}H_{44}BOPS$: C, 80.46; H, 6.41%.

Preparation of (2-Methylthiocyclopentyl)triphenylphosphonium Triflate. To a solution of cyclopentene (0.28 g, 4.0 mmol) in dichloromethane (10 mL) was added a solution of DMTST (1.03 g, 4.00 mmol) in dichloromethane (5 mL) over 30 min under nitrogen at 0°C. After stirring for 1 h, triphenylphosphine (1.05 g, 4.0 mmol) in dichloromethane (10 mL) was added to this solution at 0°C. After stirring for additional 8 h, the reaction mixture was evaporated to give a pale yellow oil. The oil was washed with diethyl ether to afford a colorless oil of 2-methylthiocyclopentenyltriphenylphosphonium trifluoromethanesulfonate, **1a'** (1.8 g, 3.5 mmol, 88%). This salt was converted into the corresponding tetraphenylborate by treatment with sodium tetraphenylborate. Mp 230—231°C; ^{1}H NMR ($CDCl_3$) δ=2.18 (s, 3H, SMe), 1.13—4,27 (m, 8H, cyclopentyl), 7.97—8.40 (m, 15H, Ph). Found: C, 82.52; H, 6.47%. Calcd for $C_{48}H_{46}BPS$: C, 82.75; H, 6.66%.

Other reactions were carried out in a similar manner.

1b': Mp 191—192°C; ^{1}H NMR ($CDCl_3$) δ=1.67 (s, 3H, SMe), 1.73—2.40 (m, 9H, cyclohexyl), 4.07—4.57 (m, 1H, CH), 7.70—8.0 (m, 15H, Ph). Found: C, 57.91; H, 5.55%. Calcd for $C_{26}H_{28}F_3O_3PS$: C, 57.77; H, 5.21%.

1c': Mp 170—171°C; ^{1}H NMR ($CDCl_3$) δ=2.12 (s, 3H, SMe), 3.23 (m, 2H, CH_2), 5.23 (m, 1H, CH), 7.04—7.27 (m, 5H, Ph), 7.56—7.70 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$) δ=15.82 (SMe), 35.16 (CH_2), 41.55 (CH), 127.9—135.38 (Ar). Found: C, 59.43; H, 4.94%. Calcd for $C_{28}H_{26}F_3O_3PS$: C, 59.78; H, 7.21%.

1d': Mp 258—259°C (as a BPh_4); ^1H NMR ($CDCl_3$) δ=1.82 (s, 3H, SMe), 0.72—4.33 (m, 14H, heptyl), 7.76—7.90 (m, 35H, Ar). Found: C, 82.37; H, 6.90%. Calcd for $C_{50}H_{52}BPS$: C, 82.63; H, 7.21%.

Preparation of Triphenyl-2-phenylthiocyclohexylphosphonium Triflate (1g). To a solution of diphenyl disulfide (2.18 g, 10 mmol) in dichloromethane (50 mL) was added a solution of methyl triflate (1.05 mL, 10 mmol) in dichloromethane (15 mL) at 0°C. After stirring for 2 h, a solution of cyclohexene (0.82 g, 10 mmol) in dichloromethane (15 mL) was added dropwise to this solution at 0°C over 1 h. After stirring for 15 h at room temperature, the reaction mixture was evaporated to give a pale purple oil, which was washed with ether (15 mL×3). To this oil was added 15 mL of dichloromethane. When 15 mL of ether was added to this solution, colorless crystals were precipitated. Recrystallization from dichloromethane–ether afforded colorless crystals of triphenyl-2-phenylthiocyclohexylphosphonium triflate, **1g** (1.65 g, 2.7 mmol, 27%); Mp 241—242°C, ^1H NMR ($CDCl_3$) δ=1.07—1.25 (m, 1H, C-4 methylene), 1.43—1.61 (m, 1H, C-6 methylene), 1.72—1.86 (m, 3H, C-5 methylene and C-4 methylene), 1.86—2.04 (m, 1H, C-2 methine), 2.22—2.36 (m, 2H, C-3 methylene), 2.50—2.68 (m, 1H, C-6 methylene), 4.36—4.54 (m, C-2 methine), 6.68—8.01 (m, 20H, C-3 methylene), 2.50—2.68 (m, 1H, C-6 methylene), 4.36—4.54 (m, C-1 methine), 6.68—8.01 (m, 20H, Ar). ^{13}C NMR ($CDCl_3$) δ=25.1 (d, C-4), 25.6 (C-5), 34.7 (d, C-1), 36.0 (C-3), 48.6 (C-2), 127.6-134.4 (Ar). Found: C, 61.85; H, 5.19%. Calcd for $C_{31}H_{30}F_3O_3PS_2$: C, 61.78; H, 5.02%.

The Reaction of 1b with Trimethyloxonium Tetrafloroborate. To a solution of the salt **1b** (0.96 g, 2 mmol) in dichloromethane (30 mL) was added trimethyloxonium tetrafloroborate (2.0 g, 1.4 mmol) in one portion. After refluxing for 2 h, the reaction mixture was evaporated to give the pale yellow crystals. Recrystallization from methanol afforded colorless crystals of 2-triphenylphosphoniocyclohexyldimethylsulfonium tetrafluoroborate, **2b** (0.88 g, 1.52 mmol, 76%). Mp 215—216°C; ^1H NMR (CD_3SOCD_3) δ=1.35—1.47 (m, 1H, C-3 methylene), 1.59—1.62 (m, 3H, C-4,6 methylene), 1.81—1.93 (m, 1H, C-3 methylene), 2.05—2.10 (m, 1H, C-5 methylene), 2.22—2.81 (m, 1H, C-6 methylene), 2.78 (s, 3H, SMe), 2.93 (s, 3H, SMe), 3.72—3.78 (m, 1H, P-CH), 4.81—4.88 (m, 1H, P-CH), 7.63—8.18 (m, 15H, Ar). ^{13}C NMR (CD_3SOCD_3) δ=19.8 (SMe), 23.0 (C-3), 23.4 (d, C-4), 23.5 (SMe), 24.2 (d, C-5), 27.5 (C-6), 32.0 (d, P-C), 51.2 (d, S-C), 116.5-135.4 (Ar). Found: C, 54.17; H, 5.43%. Calcd for $C_{26}H_{31}B_2F_8PS$: C, 53.83; H, 5.39%. 2-Triphenylphosphoniocyclopentyldimethylsulfonium tetrafloroborate, **2a**, was prepared in a similar manner. Yield, 70%. Mp 226—227°C; ^1H NMR (CD_3SOCD_3) δ=1.10—1.18 (m, 1H, methylene), 1.62—1.72 (m, 1H, C-5 methylene), 2.01—2.07 (m, 1H, C-5 methylene), 2.27—2.29 (m, 1H, C-3 methylene), 2.61—2.63 (m, 1H, C-3 methylene), 2.88 (s, 3H, SMe), 3.01 (s, 3H, SMe), 4.57—4.62 (m, 1H, S-CH), 5.01—5.04 (m, 1H, P-CH), 7.82—8.00 (m, 15H, Ar). ^{13}C NMR (CD_3SOCD_3) δ=19.8 (SMe), 22.9 (C-3), 23.4 (d, C-4), 23.5 (SMe), 24.2 (d, C-5), 27.5 (C-6), 32.0 (d, C-2), 51.2 (d, C-1), 116.5—135.4 (Ar). Found: C, 52.15; H, 5.43%. Calcd for $C_{25}H_{29}B_2F_8PS$: C, 52.03; H, 5.16%.

The Reaction of 2a with DBU. To a solution of **2a** (1.05 g, 2 mmol) in tetrahydrofuran (20 mL) was added a solution of DBU (0.32 g, 2.2 mmol) in tetrahydrofuran (10 mL) at room temperature. After stirring for 5 h, the reaction mixture was evaporated and 30 mL of water was added. The resulting suspension was extracted with dichloromethane (15 mL×3). The combined extracts were dried over magnesium sulfate and evaporated to give colorless crystals of cyclopentenyltriphenylphosphonium tetrafluoroborate, **3a** (0.62 g, 1.58 mmol, 78%). Mp 245—246°C; ^1H NMR ($CDCl_3$) δ=2.22—2.31 (m, 2H, C-4 methylene), 2.85—2.86 (m, 2H, C-5 methylene), 3.01—3.21 (m, 2H, C-3 methylene), 6.90—6.93 (m, 1H, =CH), 7.55—7.88 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=24.2 (d, C-4), 34.9 (d, C-5), 35.8 (d, C-3), 124.0 (d, C-1), 161.7 (d, C-2), 116.9—135.4 (Ar). Elemental analysis was performed by its BPh_4 salt. Mp 238—239°C. Found: C, 87.13; H, 6.42%. Calcd for $C_{47}H_{41}BP$: C, 86.96; H, 6.36%. Compound **3b** was obtained in a similar manner. Mp 248—249°C; ^1H NMR ($CDCl_3$) δ=1.80—1.83 (m, 2H, C-4 methylene), 1.83—1.87 (m, 2H, C-5 methylene), 2.25—2.26 (m, 2H, C-6 methylene), 2.50—2.65 (m, 2H, C-3 methylene), 6.75—6.81 (m, 1H, CH), 7.45—7.99 (m, 15H, Ar). Found: C, 66.73; H, 5.50%. Calcd for $C_{24}H_{24}BF_4P$: C, 67.00; H, 5.62%.

The Reaction of 1b' with DBU. To a solution of the salt **1b'** (0.51 g, 1 mmol) in dichloromethane (10 mL) was added a solution of DBU (0.16 g, 1.1 mmol) in dichloromethane (5 mL) at room temperature. After stirring for 5 h, the reaction mixture was poured into water (30 mL) and extracted with dichloromethane (10 mL×3). The combined extracts were dried over $MgSO_4$ and evaporated to give colorless crystals of vinylphosphonium salts (0.47 g, 0.94 mmol, 94% yield). Recrystallization from dichloromethane–ether afforded the pure crystals of **3b'**.

Mp 232—233°C; ^1H NMR ($CDCl_3$) δ=1.81—1.87 (m, 4H, C-4,5 methylene), 2.24—2.26 (m, 2H, C-6 methylene), 2.51—2.53 (m, 2H, C-3 methylene), 6.76—6.83 (m, 1H, =CH), 7.63—7.95 (Ar). ^{13}C NMR ($CDCl_3$) δ=20.5 (C-4), 22.1 (d, C-5), 26.6 (d, C-6), 28.0 (d, C-3), 118.6 (d, C-1), 156.3 (d, C-2), 116.6—135.4 (Ar). Found: C, 60.88; H, 5.43%. Calcd for $C_{25}H_{25}F_3O_3PS$: C, 60.85; H, 5.11%.

Compound **3a'** was prepared in a similar manner, which was converted into a BPh_4 salt.

3a': Mp 238—239°C; ^1H NMR (CD_3NO_2) δ=2.22—2.29 (m, 2H, C-4 methylene), 2.79—2.89 (m, 4H, C-3,4 methylene), 6.82—7.34 (m, 21H, C-2 methine and BPh_4), 7.71—7.93 (m, Ar). ^{13}C NMR (CD_3NO_2) δ=25.5 (d, C-4), 36.1 (d, C-5), 36.9 (d, C-3), 124.4 (C-1), 163.0 (d, C-2), 118.9-137.5 (Ar).

Preparation of Vinylphosphine Oxide. To a solution of 2-methylthiocyclohexylphosphonium tetrafluoroborate, **1b** (1.5 g, 2.78 mmol) in water (35 mL)–THF (5 mL) was added a solution of aq NaOH (20% w/v, 40 mL). After refluxing for 9 h, the reaction mixture was extracted three times with dichloromethane (25 mL). The combined extracts were dried over $MgSO_4$ and evaporated to give a pale yellow oil which crystallized upon standing. Recrystallization from MeOH–ether gave colorless crystals of cyclohexenyldiphenylphosphine oxide (**4b**). (0.73 g, 2.60 mmol, 94%); mp 72—73°C; ^1H NMR ($CDCl_3$) δ=1.63—1.77, 2.07—2.30 (m, 8H, CH_2), 6.20—6.57 (m, 1H, olefin), 7.43—7.76 (m, 10H, Ar). Found: C, 76.43; H, 6.77%. Calcd for $C_{18}H_{19}OP$: C, 76.57; H, 6.80%. Cyclopentenyldiphenylphosphine oxide (**4a**) was prepared in a similar manner. (0.59 g, 1.83 mmol, 92%); mp 88—89°C; ^1H NMR ($CDCl_3$) δ=1.87—2.23, 2.47—2.67 (m, 6H, CH_2), 6.28—6.45 (m, 1H, olefin), 7.43—7.87 (m, 10H, Ar). Found: C, 75.80; H, 6.07%. Calcd for $C_{17}H_{17}OP$: C, 76.10; H. 6.39%.

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