

a) Mp of BPh₄ salts.

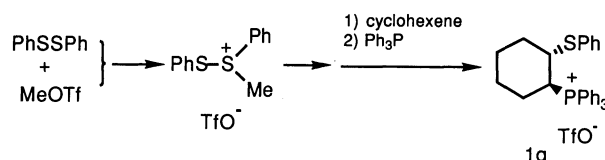
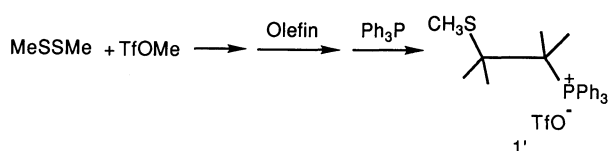
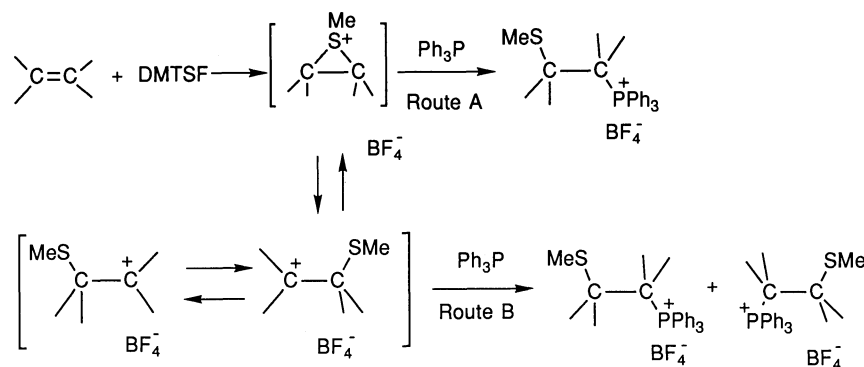


Table 2. Preparation of 2-Methylthioalkylphosphonium Salts Using of DMTST

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 BPh₄ 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 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 unsuccessful.

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 synthesis 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).

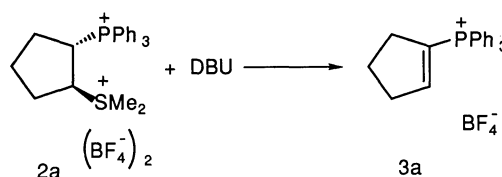
However, when **1c'** was used as a substrate, starting **1c'** was recovered almost quantitatively. Because α -hydrogen abstraction by DBU does not occur.

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.

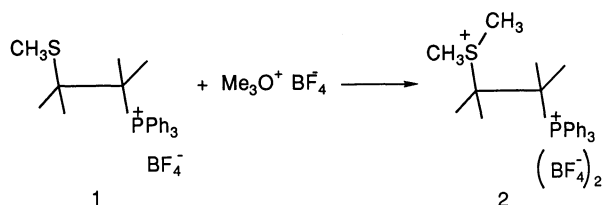
In summary, the reaction of DMTST (or DMTSF) with olefins followed by the addition of triphenylphosphine afforded the corresponding 2-methylthioalkylphosphonium salts, which were further treated with bases to give the corresponding vinylphosphonium salts or vinyl phosphine oxides. This new method provides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



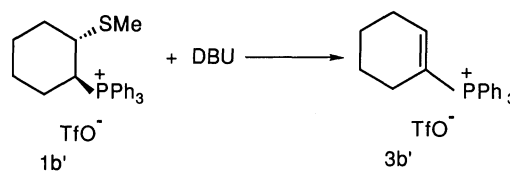
Scheme 6.

Table 4. Preparation of vinylphosphonium Salts from Phosphoniosulfonium Salts

Salt	Product	Yield	Mp
		%	$^{\circ}\text{C}$
Cyclopentyl	3a	79	245—246
Cyclohexyl	3b	76	223—224



Scheme 5.



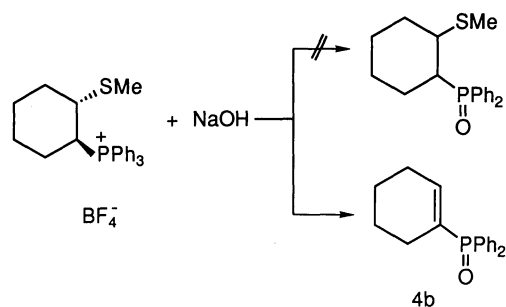
Scheme 7.

Table 3. Preparation of Phosphoniosulfonium Salts

Salt	Phosphoniosulfonium salt	Yield	Mp
		%	$^{\circ}\text{C}$
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. ^1H 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. Colorless crystals precipitated were filtered under a nitrogen atmosphere to give colorless crystals of DMTST (10.8 g, 0.042 mol, 84%): Mp $53\text{--}55^\circ\text{C}$ (lit.⁷ $28\text{--}36^\circ\text{C}$). ^{13}C NMR (CD_3NO_2) $\delta=17.8$ (SMe), 32.0 (Me).

Preparation of 2-Methylthiocyclopentyltriphenylphosphonium Tetrafluoroborate (1a). To a solution of DMTST (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. $126\text{--}127^\circ\text{C}$. ^1H NMR (CDCl_3) $\delta=1.43\text{--}1.50$ (m, 1H, C-3 methylene), $1.51\text{--}1.58$ (m, 1H, C-4 methylene), $1.74\text{--}1.81$ (m, 1H, C-5 methylene), $1.83\text{--}1.90$ (m, 1H, C-3 methylene), $1.90\text{--}1.96$ (m, 1H, C-4 methylene), 2.24 (s, 3H, SMe), $2.56\text{--}2.66$ (m, 1H, C-5 methylene), $3.12\text{--}3.20$ (m, 1H, S-CH), $3.75\text{--}3.84$ (m, 1H, P-

CH), $7.52\text{--}7.85$ (m, 15H, Ar). ^{13}C NMR (CDCl_3) $\delta=15.1$ (SMe), 24.4 (C-4), 28.9 (d, C-5), 33.8 (d, C-3), 37.2 (d, C-1), 47.3 (C-2), $117.4\text{--}135.6$ (Ar). Found: C, 61.73; H, 5.80%. Calcd for $\text{C}_{24}\text{H}_{26}\text{BF}_4\text{PS}$: C, 62.08; H, 5.66%. Other phosphonium salts **1b–h** were prepared in a similar manner. 2-Methylthiocyclohexyltriphenylphosphonium fluoroborate (**1b**): Mp $223\text{--}224^\circ\text{C}$. ^1H NMR (CDCl_3) $\delta=1.22\text{--}1.36$ (m, 1H, C-4 methylene), $1.42\text{--}1.48$ (m, 1H, C-6 methylene), 1.64 (s, 3H, SMe), $1.80\text{--}2.09$ (m, 7H, C-2 methine, C-3,4, and 5 methylene), $2.17\text{--}2.21$ (m, 1H, C-6 methylene), $4.15\text{--}4.24$ (m, 1H, C-1 methine), $7.59\text{--}7.77$ (m Ar), $7.79\text{--}7.97$ (m, Ar). ^{13}C NMR (CDCl_3) $\delta=14.0$ (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), $119.0\text{--}134.2$ (Ar). Found: C, 62.88; H, 60.9%. Calcd for $\text{C}_{25}\text{H}_{28}\text{BF}_4\text{PS}$: C, 62.77; H, 5.91%.

1c: Mp $198\text{--}199^\circ\text{C}$; ^1H NMR (CDCl_3) $\delta=2.07$ (s, 3H, Me), 3.27 (m, 2H, CH_2), 5.05 (m, 1H, CH), $7.06\text{--}7.75$ (m, 20H, Ph). Found: C, 64.70; H, 5.13%. Calcd for $\text{C}_{27}\text{H}_{26}\text{BF}_4\text{PS}$: C, 64.81; H, 5.25%.

1d: Mp $118\text{--}119^\circ\text{C}$; ^1H NMR (CDCl_3) $\delta=0.74\text{--}3.79$ (m, 14H, heptyl), 1.83 (s, 3H, SMe), $7.72\text{--}7.83$ (m, 15H, Ph). Found: C, 63.06; H, 6.35%. Calcd for $\text{C}_{26}\text{H}_{31}\text{BF}_4\text{PS}$: C, 62.39; H, 6.35%.

1e: Mp $131\text{--}132^\circ\text{C}$; ^1H NMR (CDCl_3) $\delta=2.19$ (s, 3H, SMe), 2.28 (s, 3H, Me), 2.52 (s, 2H, CH_2), $7.65\text{--}8.69$ (m, 20H, Ar). ^{13}C NMR (CDCl_3) $\delta=17.6$ (SMe), 21.6 (Me), 26.2 (d, P-C), 42.3 (CH_2), $115.3\text{--}135.38$ (Ar). Found: C, 65.41; H, 5.55%. Calcd for $\text{C}_{28}\text{H}_{26}\text{BF}_4\text{PS}$: C, 65.38; H, 5.50%.

1f: Mp $240\text{--}241^\circ\text{C}$; ^1H NMR (CD_3SOCD_3) $\delta=1.81$ (s, 3H, SMe), $2.54\text{--}2.79$ (m, 1H, CH), $3.16\text{--}4.11$ (m, 2H, P- CH_2), $5.06\text{--}5.28$ (m, 2H, CH_2), $6.85\text{--}7.70$ (BPh₄), $7.74\text{--}7.82$ (15H, Ph). ^{13}C NMR (CDCl_3) $\delta=13.8$ (SMe), 24.4 (d, CH), 42.7 (d, CH_2), 64.2 (d, P- CH_2), $121.5\text{--}135.7$ (Ar). Found: C, 80.86; H, 6.86%. Calcd for $\text{C}_{46}\text{H}_{44}\text{BOPS}$: 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 $230\text{--}231^\circ\text{C}$; ^1H NMR (CDCl_3) $\delta=2.18$ (s, 3H, SMe), $1.13\text{--}4.27$ (m, 8H, cyclopentyl), $7.97\text{--}8.40$ (m, 15H, Ph). Found: C, 82.52; H, 6.47%. Calcd for $\text{C}_{48}\text{H}_{46}\text{BPS}$: C, 82.75; H, 6.66%.

Other reactions were carried out in a similar manner.

1b': Mp $191\text{--}192^\circ\text{C}$; ^1H NMR (CDCl_3) $\delta=1.67$ (s, 3H, SMe), $1.73\text{--}2.40$ (m, 9H, cyclohexyl), $4.07\text{--}4.57$ (m, 1H, CH), $7.70\text{--}8.0$ (m, 15H, Ph). Found: C, 57.91; H, 5.55%. Calcd for $\text{C}_{26}\text{H}_{28}\text{F}_3\text{O}_3\text{PS}$: C, 57.77; H, 5.21%.

1c': Mp $170\text{--}171^\circ\text{C}$; ^1H NMR (CDCl_3) $\delta=2.12$ (s, 3H, SMe), 3.23 (m, 2H, CH_2), 5.23 (m, 1H, CH), $7.04\text{--}7.27$ (m, 5H, Ph), $7.56\text{--}7.70$ (m, 15H, Ph). ^{13}C NMR (CDCl_3) $\delta=15.82$ (SMe), 35.16 (CH_2), 41.55 (CH), $127.9\text{--}135.38$ (Ar). Found: C, 59.43; H, 4.94%. Calcd for $\text{C}_{28}\text{H}_{26}\text{F}_3\text{O}_3\text{PS}$: C, 59.78; H, 7.21%.

1d': Mp 258–259°C (as a BPh₄); ¹H NMR (CDCl₃) 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 C₅₀H₅₂BPS: 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 (CDCl₃) 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). ¹³C NMR (CDCl₃) 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 C₃₁H₃₀F₃O₃PS₂: C, 61.78; H, 5.02%.

The Reaction of 1b with Trimethyloxonium Tetrafluoroborate. To a solution of the salt **1b** (0.96 g, 2 mmol) in dichloromethane (30 mL) was added trimethyloxonium tetrafluoroborate (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 (CD₃SOCD₃) 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). ¹³C NMR (CD₃SOCD₃) 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 C₂₆H₃₁B₂F₈PS: C, 53.83; H, 5.39%. 2-Triphenylphosphoniocyclopentylidimethylsulfonium tetrafluoroborate, **2a**, was prepared in a similar manner. Yield, 70%. Mp 226–227°C; ¹H NMR (CD₃SOCD₃) 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). ¹³C NMR (CD₃SOCD₃) 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 C₂₅H₂₉B₂F₈PS: 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 (CDCl₃) 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). ¹³C NMR (CDCl₃) 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 BPh₄ salt. Mp 238–239°C. Found: C, 87.13; H, 6.42%. Calcd for C₄₇H₄₁BP: C, 86.96; H, 6.36%. Compound **3b** was obtained in a similar manner. Mp 248–249°C; ¹H NMR (CDCl₃) 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 C₂₄H₂₄BF₄P: 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 MgSO₄ 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 (CDCl₃) 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). ¹³C NMR (CDCl₃) 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 C₂₅H₂₅F₃O₃PS: C, 60.85; H, 5.11%.

Compound **3a'** was prepared in a similar manner, which was converted into a BPh₄ salt.

3a': Mp 238–239°C; ¹H NMR (CD₃NO₂) 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 BPh₄), 7.71–7.93 (m, Ar). ¹³C NMR (CD₃NO₂) 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 MgSO₄ 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 (CDCl₃) δ=1.63–1.77, 2.07–2.30 (m, 8H, CH₂), 6.20–6.57 (m, 1H, olefin), 7.43–7.76 (m, 10H, Ar). Found: C, 76.43; H, 6.77%. Calcd for C₁₈H₁₉OP: C, 76.57; H, 6.80%. Cyclopentenylidiphenylphosphine oxide (**4a**) was prepared in a similar manner. (0.59 g, 1.83 mmol, 92%); mp 88–89°C; ¹H NMR (CDCl₃) δ=1.87–2.23, 2.47–2.67 (m, 6H, CH₂), 6.28–6.45 (m, 1H, olefin), 7.43–7.87 (m, 10H, Ar). Found: C, 75.80; H, 6.07%. Calcd for C₁₇H₁₇OP: C, 76.10; H, 6.39%.

References

- 1) G. J. O'Malley and M. P. Cava, *Tetrahedron Lett.*, **26**, 6159 (1985). J. K. Kim, J. K. Pau, and M. C. Caserio, *J. Org. Chem.*, **44**, 1544 (1979).
 - 2) K. Okuma, T. Koike, S. Yamamoto, K. Yonekura, and H. Ohta, *Chem. Lett.*, **1989**, 1953.
 - 3) G. K. Helmkamp and D. J. Pettitt, *Org. Synth.*, **46**, 122 (1966).
 - 4) H. Meerwein, K. F. Zenner, and R. Gipp, *Ann.*, **688**, 67 (1965).
 - 5) S. H. Smallcombe and M. C. Caserio, *J. Am. Chem. Soc.*, **93**, 5826 (1971). M. C. Caserio and J. K. Kim, *J. Am. Chem. Soc.*, **104**, 3231 (1982).
 - 6) B. M. Trost and T. Shibata, *J. Am. Chem. Soc.*, **104**, 3225 (1982). B. M. Trost, T. Shibata, and S. J. Martin, *J. Am. Chem. Soc.*, **104**, 3228 (1982). B. M. Trost and T. Sato, *J. Am. Chem. Soc.*, **107**, 719 (1985).
 - 7) M. Ravenscroft, R. M. G. Roberts, and J. G. Tillett, *J. Chem. Soc., Perkin Trans. 2*, **1982**, 1569. P. Fügedi and P. J. Garegg, *Carbohydr. Res.*, **149**, C9 (1986).
 - 8) For example, see H. Meerwein, *Org. Synth.*, Coll. Vol. V, 1080 and 1096 (1973). C. R. Johnson, J. J. Rigau, M. Haake, D. McCants, Jr., J. E. Keiser, and A. Gertsema, *Tetrahedron Lett.*, **1968**, 3719. C. R. Johnson, and C. W. Schroeck, *J. Am. Chem. Soc.*, **90**, 6852 (1968). H. W. Heine, T. A. Newton, G. J. Blossick, C. Meyer, and G. B. Corcoran, III, *J. Org. Chem.*, **38**, 651 (1973). K. Okuma, N. Higuchi, H. Ohta, and M. Kobayashi, *Chem. Lett.*, **1980**, 1503. K. Okuma, Y. Tanaka, and H. Ohta, *J. Am. Chem. Soc.*, **103**, 5976 (1981). K. Okuma, K. Nakanishi, and H. Ohta, *J. Org. Chem.*, **49**, 1402 (1984). N. A. Lebel and N. Balasubramanian, *Tetrahedron Lett.*, **26**, 4331 (1985). K. Okuma, N. Higuchi, S. Kaji, H. Takeuchi, H. Ohta, H. Matsuyama, N. Kamigata, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **63**, 3323 (1990).
 - 9) For a review, see B. M. Trost and L. S. Melvin, Jr., "Sulfur Ylides," Academic Press, New York (1975). E. Block, "Reactions of Organosulfur Compounds," Academic Press, New York (1978), Chap. 3.
 - 10) J. M. McIntosh and R. S. Steevensz, *Can. J. Chem.*, **55**, 2442 (1977). E. E. Schweizer, *J. Am. Chem. Soc.*, **86**, 2744 (1964). R. J. Hinkle, P. J. Stang, and M. H. Kowalski, *J. Org. Chem.*, **55**, 5033 (1990). M. H. Kowalski, R. J. Hinkle, and P. J. Stang, *J. Org. Chem.*, **54**, 2783 (1989). For a review, see T. Minami and I. Yamamoto, *Rev. Heteroatom Chem.*, **5**, 270 (1991).
 - 11) T. Minami, H. Sako, T. Ikehara, T. Hanamoto, and I. Hirao, *J. Org. Chem.*, **48**, 2569 (1983). Y. Okada, T. Minami, S. Yahiro, and K. Akinaga, *J. Org. Chem.*, **54**, 974 (1989).
 - 12) E. Vedejs, K. A. J. Snoble, and P. L. Fuchs, *J. Org. Chem.*, **38**, 1178 (1973).
 - 13) G. Saleh, T. Minami, Y. Ohshiro, and T. Agawa, *Chem. Ber.*, **112**, 355 (1979). See also J. R. Shutt and S. Tripett, *J. Chem. Soc. C*, **1969**, 2038.
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