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Reaction of Olefins with Dimethylthiomethylsulfonium Salts and Triphenylphosphine. A New Convenient Synthesis of Vinylphosphonium Salts

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Olefins were effectively converted to the corresponding 2-methylthioalkylphosphonium salts by the reaction with dimethylthiomethylsulfonium salts and triphenylphosphine. The reaction of these salts with bases gave vinylphosphonium salts or vinylphosphine oxides in good yields.

Dimethylthiomethylsulfonium fluoroborate (DMTSF) is a useful reagent for the intramolecular cyclization of unsaturated thioketals.[1] Trost et al. showed that the reaction of DMTSF with olefins afforded corresponding 2-(methylthio)alkylsulfonium salts, which were further treated with nucleophiles to give 2-(methylthio)alkyl derivatives.[2] However, there is no report on the synthesis of 2-(methylthio)alkylphosphonium salts **1** from DMTSF. In our recent research, we revealed that the reaction of epoxides with triphenylphosphine in the presence of strong acids gave 2-(hydroxy)alkylphosphonium salts in good yields.[3] This result, in turn, prompted us to investigate further utilization of DMTSF and possibility of the formation of **1**. In this communication, we would like to report a new convenient synthesis and reaction of vinylphosphonium salts **2** and vinylphosphine oxides **3** via phosphonium salts **1**.

A typical reaction was run as follows: To a suspension of DMTSF (5 mmol) in dichloromethane (25 mL) was added at 0 °C a solution of cyclopentene (5 mmol) in dichloromethane at 0 °C. After stirring for 2 h, triphenylphosphine (5 mmol) in dichloromethane (15 mL) was added to this solution. The resulting solution was evaporated to give pale yellow crystals. Recrystallization from methanol gave colorless crystals of [2-(methylthio)cyclopentyl]triphenylphosphonium fluoroborate (**1a**) in 85.8% yields. Other reactions were carried out in a similar manner (Table 1).

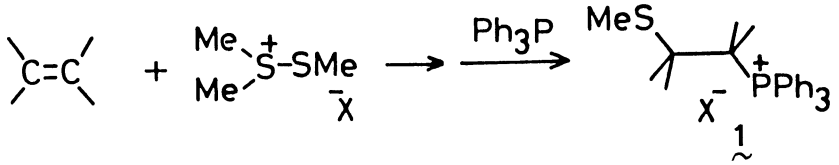
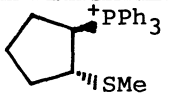
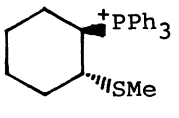
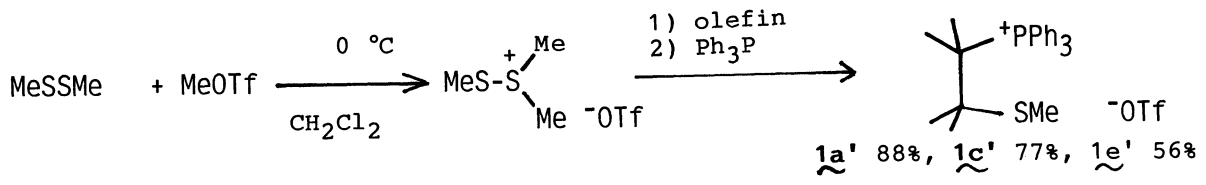


Table 1. Preparation of [2-(Methylthio)alkyl]triphenylphosphonium salts (1)

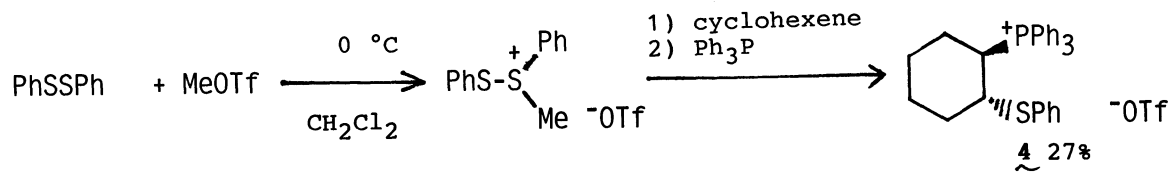
Olefin	Product		Yield/%	Mp/°C
cyclopentene	1a	 $^-BF_4$	86	126-127
cyclohexene	1b	 $^-BF_4$	85	223-224
styrene	1c	$PhCH(^+PPh_3)CH_2SMe$ $^-BF_4$	90	198-199
1-heptene	1d	$CH_3(CH_2)_4CH(SMe)CH_2{}^+PPh_3$ $^-BF_4$	93	118-119
1-methylstyrene	1e	$PhC(Me)(^+PPh_3)CH_2SMe$ $^-BF_4$	82	132-133
allyl alcohol	1f	$HOCH_2CH(SMe)CH_2{}^+PPh_3$ $^-BF_4$	38	240-241[a]

a) Mp was determined as a tetraphenylborate.

We also found that solutions of methyl trifluoromethanesulfonate (MeOTf) and dimethyl disulfide (or diphenyl disulfide) are also effective to produce 2-methylthio- **1** or [2-(phenylthio)alkyl]phosphonium salts **4**, respectively.[4]



1a' 88%, 1c' 77%, 1e' 56%



4 27%

The reaction is not only regioselective but also stereoselective. The stereochemistry of the addition is trans, as has been shown for cyclopentene and cyclohexene.[5] As to the formation of phosphonium salts **1**, following two mechanisms are possible: treatment of olefin with DMTSF formed the corresponding episulfonium ion, which was directly attacked by triphenylphosphine to give **1** (Route A); the episulfonium ion was transformed to carbocation which resulted in the formation of **1** (Route B).

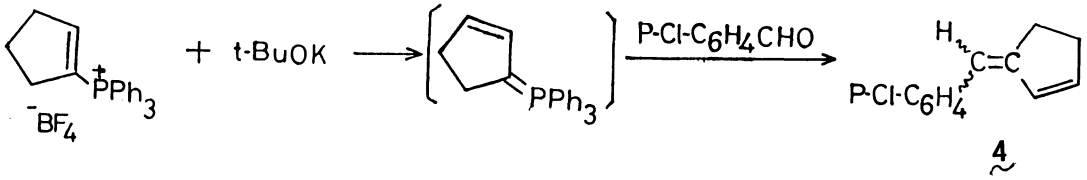
The trans stereoselectivity observed in the reactions of cyclohexene and cyclopentene and the regioselectivity observed in the reactions of 1-hexene, 1-heptene, and allyl alcohol, in which triphenylphosphine attached to the less hindered methylene carbon, suggested that the reaction would proceed in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

Although the synthesis and reaction of 2-(hydroxy)alkylphosphonium salts or 2-(phenoxy)alkylphosphonium salts have been investigated widely because of their versatile synthetic utility,[6] there are a few reports on the synthesis

of **1**.[7,8] Thus, in order to investigate the utilization of these phosphonium salts, we have treated them with various bases and aldehydes to find a procedure leading to 2-thiomethylated olefins. The reaction of **1a** with butyllithium followed by the addition of benzaldehyde, however, afforded the corresponding vinyl phosphonium salts (**2a**) in 68% yields. This result indicated that the 2-(methylthio)alkylphosphonium ylide obtained was unstable and eliminated the methylthio group very easily. When diazabicyclo[5.4.0]undecene (DBU) was used as a base, the yield of this reaction was raised to 95%. We also found that the reaction of **1a** with aqueous sodium hydroxide afforded (1-cyclopentenyl)-diphenylphosphine oxide in 87.5% yield.

Unsubstituted vinylphosphonium bromide, which was prepared by the reaction of 2-bromophenethole or 2-halo alcohol with triphenylphosphine,[9] is a useful reagent for the synthesis of heterocyclic compounds.[10] However, substituted **2** were generally difficult to synthesize, which were previously prepared by the reaction of phosphonium ylides with phenylselenyl bromide followed by oxidation.[11] The present method has many advantages: 1) the reaction is clean, 2) the yields are generally higher than the above method, 3) this reaction can be carried out in one-pot procedure.

We then tried the reaction of **2a**. The reaction of **2a** with potassium tert-butoxide followed by the addition of p-chlorobenzaldehyde afforded a mixture of Z- **4a** and E-dienes **4b** (ratio=2:5).[12]



4

The initial stage of the present reaction is proton abstraction of **2a**. Previously, several workers tried the reaction of vinylphosphonium salts with bases. Minami et al. reported that the reaction of cyclobutenylphosphonium perchlorate with alkoxide followed by the addition of benzaldehyde afforded 1-benzylidene-2-ethoxycyclobutane.[11] Schweizer et al. also reported that vinylphosphonium bromide reacted with bases followed by the addition of piperidine and benzaldehyde to give a mixture of cis- and trans-cinnamylpiperidine.[7] A similar γ-proton abstraction of vinyl phosphonium salts was reported. Vedejs et al. found that the reaction of [2-(hydroxy)cycloheptenyl]methyldiphenylphosphonium fluoroborate with DBU gave the corresponding vinylphosphonium salts accompanied with cycloheptene, which further reacted with DBU and benzaldehyde to afford dienes.[13]

Thus, 2-(methylthio)alkylphosphonium salts have been proved to be a versatile precursor for the vinylphosphonium salts, which can be utilized for the synthesis of dienes by treatment of a base and aldehyde.

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5) Stereochemistry of the products was determined by their NMR spectra. For example, the vicinal methine coupling constant of **1a** is 5.5 Hz, which suggested trans conformation.

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12) ^{1}H NMR spectra of **4**: **4a**; ($CDCl_3$) δ 2.53 (m, 2H), 2.69 (m, 2H), 6.15 (br s, 1H, ArC<u>H</u>=), 6.34 (m, 1H), 6.69 (m, 1H), 7.21 (q, 4H). **4b**; ($CDCl_3$) δ 2.67 (m, 2H), 2.81 (m, 2H), 6.18 (m, 1H), 6.27 (m, 1H), 6.29 (br s, 1H, ArC<u>H</u>=), 7.25 (s, 4H).

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