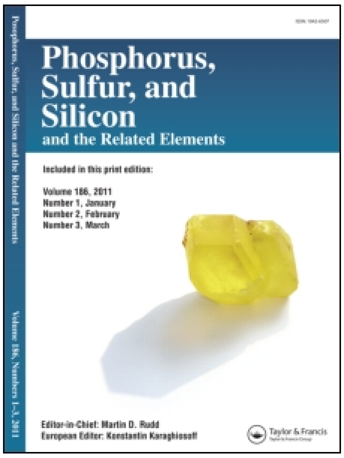

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REACTIONS OF DIMETHYLVINYLSULFONIUM SALTS WITH SODIUM PHENOXIDE

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Synthesis of vinyl sulfides by reaction of dimethylvinylsulfonium salts with sodium phenoxide is reported. Dependence of reactivity on substituents is discussed.

INTRODUCTION

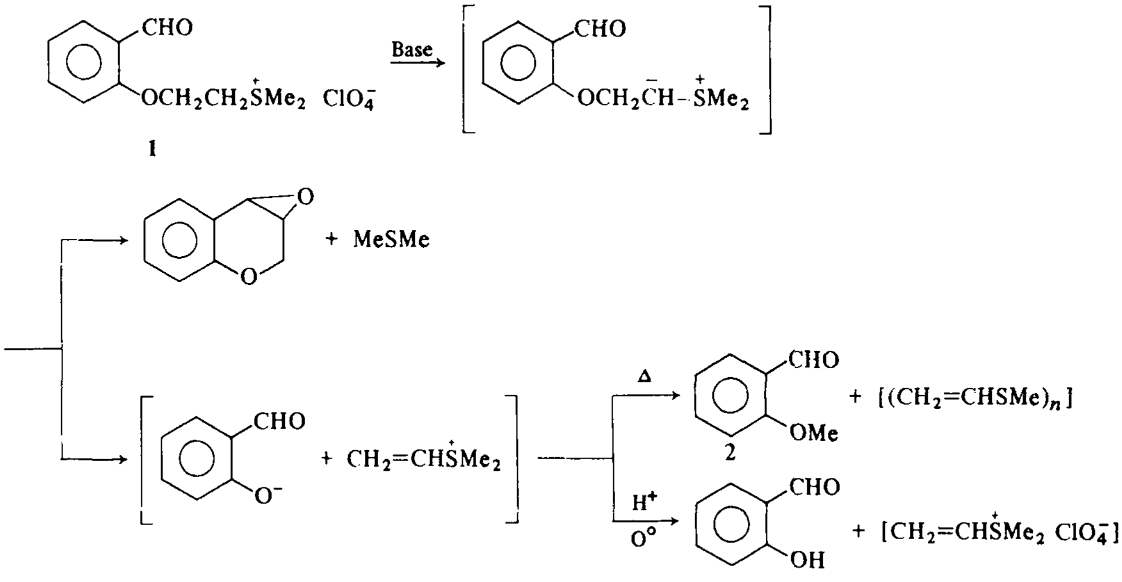
Vinyl sulfides have recently become very important reagents since they serve as convenient precursors[1] to aldehydes and ketones. Accordingly it is useful to develop simple preparative methods for them. They are generally synthesized by dehydrohalogenation[2] of halogenated sulfides and by alkylthiomethylenation of aldehydes and ketones by using alkylthiomethylenephosphoranes[3] and alkylthiophosphonate anions.[3]

Although applications of phosphorus ylides for synthesis of heterocyclic compounds via intramolecular Wittig reactions[4] have been widely studied, little is known about the corresponding reactions of sulfur ylides. In the course of studies of sulfonium ylides from such a point of view, we have observed that arylethenyldimethylsulfonium salts are easily demethylated by a phenoxy anion to generate arylethenylmethyl sulfides.

We now wish to report reactions of dimethylvinylsulfonium salts with sodium phenoxide.

RESULTS AND DISCUSSION

When a solution of 2-(*o*-formylphenoxy)ethyldimethylsulfonium perchlorate (1) in THF was refluxed for 24 hr in the presence of sodium hydride, only *o*-anisaldehyde (2) was obtained in 33% yield.

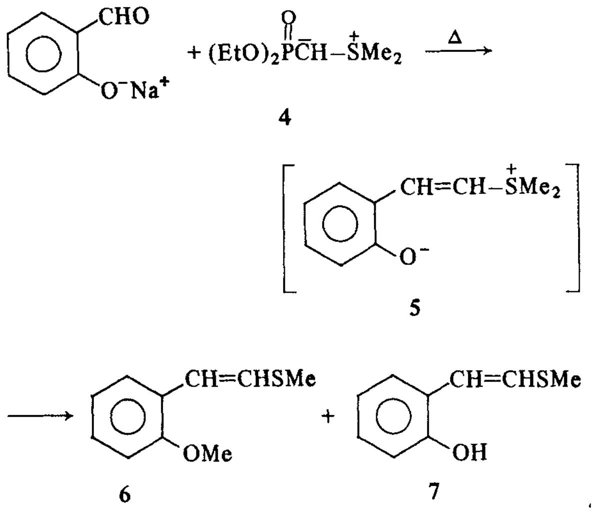


Scheme 1

On the other hand, treatment of the solution with *n*-butyllithium at 0° for 4 hr gave salicylaldehyde (3) in 50% yield. Thus, regardless of the reaction conditions employed, the expected cyclization was not observed (Scheme 1).

The formation of 2 could be explained in terms of methylation of an *o*-formylphenoxy anion with the dimethylvinylsulfonium moiety, which would be generated by elimination of the *o*-formylphenoxy anion from the intermediate sulfur ylide, as shown in scheme 1.

In the reaction of sodium salicylaldehyde with (diethoxyphosphinylmethylene)dimethylsulfurane (4) at THF refluxing temperature for 14 hr, *o*-methoxyphenylethenyl methyl sulfide (6, *trans:cis*=5:1 by nmr) and *o*-hydroxyphenylethenyl methyl sulfide (7, *trans:cis*=3:2 by nmr) were similarly isolated in 32 and 27% yields, respectively. On the basis of Kondo and coworker's results,[5] it is reasonable to consider that the sulfurane 4 reacted not as a sulfonium ylide but as a phosphonate carbanion with sodium salicylaldehyde to yield an intermediate sulfonium betaine 5, followed by methyl migration to a phenoxy moiety to give 6 (Scheme 2).



Scheme 2

Hence it is of interest and value to extend this type of demethylation reaction of vinylsulfonium salts with a phenoxy anion to preparation of vinyl sulfides.

Dimethylstyrylsulfonium perchlorate (8), which was prepared from the sulfurane 4 and benzaldehyde, was refluxed in THF for 13 hr together with sodium phenoxide to give *trans*-styryl methyl sulfide (9) and anisole in 70 and 45% yields.

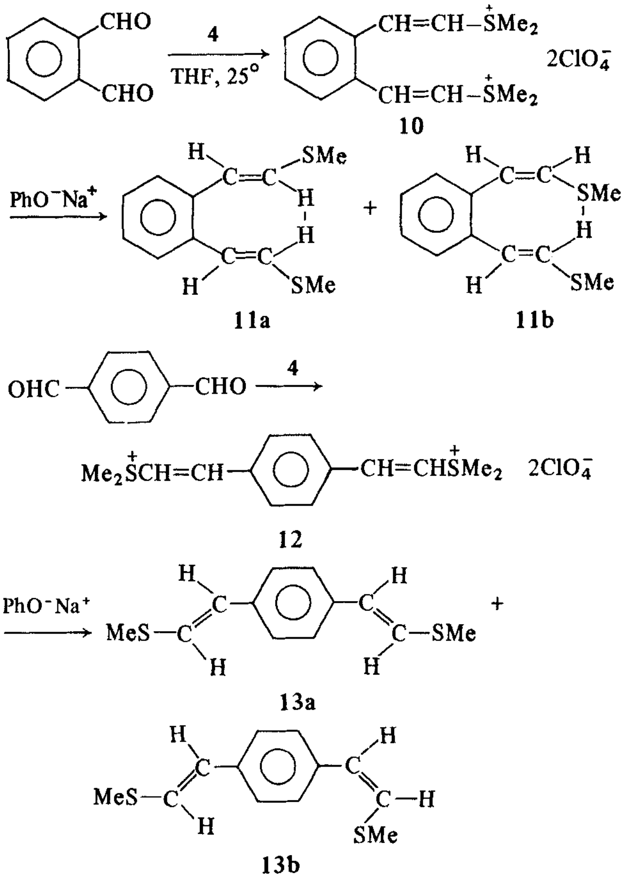
Similar treatment of bis(*o*-xylidenemethyl)dimethylsulfonium perchlorate (10) with sodium phenoxide resulted in the formation of a mixture of bis(*trans, trans-o*-xylidenemethyl)-(11a) and bis(*trans,cis-o*-xylidenemethyl) methyl sulfides (11b), of ratio which was approximately 10:1 by nmr, in 53% yield.

In contrast, the reaction of *o*-phthalaldehyde with a diethyl methylthiomethyl phosphonate carbanion did not afford the expected sulfides, 11a and 11b, under similar conditions.

On the other hand, the reaction with methylthiomethylenetriphenylphosphorane yielded expectedly a mixture of 11a and 11b, of ratio about 2:5 by nmr, in 50% yield.

Accordingly, in comparison with the phosphonate carbanion and the phosphorane, it seems to be rather favorable to use the method for the synthesis of vinyl sulfides *via* vinylsulfonium salts and sodium phenoxide in both yields and stereospecificity.

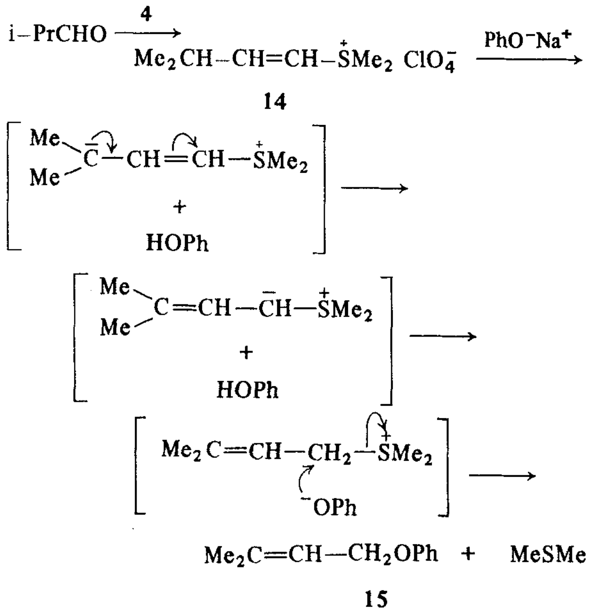
In the case of bis(*p*-xylidenemethyl)dimethylsulfonium perchlororate (12), the corresponding *trans,trans*-(13a) and *trans,cis*-sulfides (13b) were



Scheme 3

similarly obtained in 24.4 and 1.7% yields, respectively.

However, the reaction of 3-methylbutenyldimethylsulfonium perchlorate (**14**) with sodium phenoxide gave 2-methyl-4-phenoxy-2-butene (**15**) in 42% yield instead of the expected 3-methylbutenyl methyl sulfide.



Scheme 4

The formation of **15** could be reasonably explained by a sequence of abstraction of a fairly acidic γ-hydrogen of the salt **14** by a phenoxy anion, isomerization to dimethyl(2-methylpropenyl)methylenesulfurane and abstraction of a phenolic hydrogen with the above sulfurane, followed by substitution of the dimethylsulfonium group for the resulting phenoxy group, as shown in Scheme 4.

Thus, the chemical reactivities of vinylsulfonium salts to sodium phenoxide are dependent upon the substituents of the salts.

EXPERIMENTAL SECTION[6]

Materials. (Diethoxyphosphinylmethyl)dimethylsulfonium perchlorate was prepared from diethoxyphosphinylmethyl methyl sulfide and methyl iodide in the presence of silver perchlorate according to the established procedure.[5] 2-(*o*-Formylphenoxy)ethyldimethylsulfonium perchlorate was similarly synthesized from 2-(*o*-formylphenoxy)ethyl methyl sulfide [bp 130–131° (1 mm); ir(neat) 1680 (C=O) cm^{-1}; nmr (CCl_4) δ 2.18 (s, 3H, CH_3S), 2.85 (t, 2H, $-CH_2S-$), 4.12 (t, 2H, $-OCH_2-$), 6.80-7.80 (m, 4H, aromatic protons) and 10.37 (s, 1H, CHO)], and methyl iodide in quantitative yield: mp 143–144° (from ethanol); ir (Nujol) 1660 and 1650 cm^{-1} (C=O); nmr (DMSO-d_6) δ 3.05 (s, 6H, $-\overset{+}{S}Me_2$), 3.86 (t, 2H, $-CH_2O-$), 4.65 (t, 2H, $-CH_2\overset{+}{S}<$), 7.00–7.83 (m, 4H, aromatic protons) and 9.90 (s, 1H, CHO).

Preparation of Dimethylvinylsulfonium Salts. To sodium hydride (50%, 2.0 g, 0.04 mol) in 100 ml of dry tetrahydrofurane was added (diethoxyphosphinylmethyl)dimethylsulfonium perchlorate (12.5 g, 0.04 mol) with stirring. After the addition, the solution was stirred at 50–60°'for 30 min until gas evolution had ceased. To the resulting yellow solution were added equimolecular carbonyl compounds.

Yields and mp of dimethylvinylsulfonium salts obtained in the above reactions are given in Table 1.

Reaction of 2-(o-Formylphenoxy)ethyldimethylsulfonium perchlorate (**1**) *in the Presence of Base.* To a suspension of the sulfonium salt **1** (3.10 g, 0.01 mol) in 50 ml of dry THF was added sodium hydride (0.48 g, 0.01 mol; 50% in mineral oil) and the solution was refluxed with stirring for 24 hr. The reaction mixture was concentrated *in vacuo* and the resulting solid and black polymeric product was removed by filtration. The filtrate was poured into water and extracted with ether, followed by drying over Na_2SO_4. After removal of solvent ether, the residue was distilled *in vacuo* to give 0.45 g (33%) of *o*-anisaldehyde (**2**).

The similar reaction using *n*-butyllithium as base at 0° for 4 hr gave salicylaldehyde (**3**) in 50% yield.

Reaction of (Diethoxyphosphinylmethylene)dimethylsulfurane (**4**) *with Sodium salicylaldehyde.* A mixture of 4 (0.04 mol) and sodium salicylaldehyde (5.76 g, 0.04 mol) in dry THF (150 ml) was refluxed for 14 hr. The mixture was then concentrated, neutralized with aq hydrochloric acid, extracted with ether, and chromatographed on silica gel to

TABLE I

Vinylsulfonium salts from aldehydes and (diethoxyphosphinylmethylene)dimethylsulfurane (4)

Vinylsulfonium salts	Yields %	Mp °C	Empirical formula[a]
10	96.5	90	$C_{14}H_{20}Cl_2O_8S_2$
12	100	205	$C_{14}H_{20}Cl_2O_8S_2$
14	83	135–137	$C_7H_{15}ClO_4S$

[a] Satisfactory analytical data (±0.4% for C, H) were found for all compounds in the table.

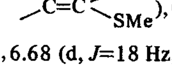
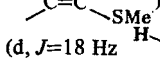
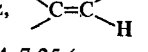
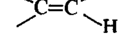
TABLE II

Reaction products[a] of vinylsulfonium salts with sodium phenoxide

Products		Yields %	Mp(bp) °C	Configuration *trans,trans*:*trans,cis*
$C_6H_5CH{=}CHSMe$	(9)	70	73 (2 mm)	*trans* only
o-$C_6H_4(CH{=}CHSMe)_2$	(11)	53	128 (3 mm)	10:1
p-$C_6H_4(CH{=}CHSMe)_2$	(13a)	24.4	140–140.5	*ca.* 14:1
	(13b)	1.7	viscous liquid	
$Me_2C{=}CHCH_2OPh$	(15)	42	110 (18 mm)	–

[a] Satisfactory analytical data (±0.4% for C, H) were found for all compounds except for the compound **13b** in the table.

give 2.31 g (32%) of *o*-methoxyphenylethenyl methyl sulfide (6) and 1.80 g (27%) of *o*-hydroxyphenylethenyl methyl sulfide (7). Pure samples of 6 and 7 were obtained by distillation. Each of them was a mixture of two isomeric *trans* and *cis* olefins whose ratios are 5:1 and 3:2 by nmr.

The product 6 had bp 92–95° (2 mm); n_D^{20} 1.6085; ir (neat) 1590 cm^{-1} (C=C); mass spectrum (70 eV) *m/e* 180 (M^+); nmr (CCl_4) δ 2.25 (s, *cis*-SCH_3), 2.30 (s, *trans*-SCH_3), 3.75 (s, 3H, OCH_3), 6.0 (d, *J*=10 Hz, ), 6.37 (d, *J*=10 Hz, ), 6.68 (d, *J*=18 Hz, ), 6.75 (d, *J*=18 Hz ), 6.54–7.25 (m, aromatic protons).

Anal. Calcd for $C_{10}H_{12}OS$: C, 66.67; H, 6.71. Found: C, 66.90; H, 6.99.

The product 7 had bp 100–105° (2 mm); n_D^{20} 1.5988; ir (neat) 3300 cm^{-1} (OH); mass spectrum (70 eV) *m/e* 166 (M^+); nmr (CCl_4) δ 2.20 (s, *cis*-SMe), 2.30 (s, *trans*-SMe), 5.40 (broad, OH), 5.70 and 5.80 (2xd, *J*=9 Hz, *cis* olefinic protons), 6.70 and 6.90 (2xd, *J*=18 Hz, *trans* olefinic protons), and 6.50–7.30 (m, aromatic protons).

Anal. Calcd for $C_9H_{10}OS$: C, 65.05; H, 6.07. Found: C, 65.44; H, 6.22.

Reaction of Bis(o-xylidenemethyl)dimethylsulfonium Perchlorate (**10**) *with Sodium Phenoxide.* A mixture of **10** (2.30 g, 5.1 mmol), and sodium phenoxide (1.80 g, 10.2 mmol) in dry THF (100 ml) was refluxed for 14 hr. The reaction mixture was concentrated, and then the residue was extracted with ether, followed by washing with water and drying over sodium sulfate. After removal of ether, the residue was chromatographed on silica gel to give anisole (0.50 g, 46%), and a mixture of bis(*trans, trans-o*-xylidenemethyl)-(**11a**) and bis(*trans,cis-o*-xylidenemethyl)methyl sulfide (**11b**) (0.61 g, 53%).

Distillation of crude **11** gave the pure sample containing **11a** and **11b** in the ratio of 10:1 by nmr: bp 128° (3 mm); ir (neat) 1580 cm^{-1} (C=C); mass spectrum (70 eV) *m/e* 222 (M^+), 175 (M^+–SMe) and 128 (M^+–2SMe); nmr (CCl_4) δ 2.40 (s, 6H, SMe), 6.35 and 6.75 (2xd, *J*=10.5 Hz, *cis* olefinic protons), 6.75 (s, *trans* olefinic protons), and 7.00–7.50 (m, 4H, aromatic protons).

Anal. Calcd for $C_{12}H_{14}S_2$: C, 64.81; H, 6.35. Found: C, 64.69 H, 6.28.

Preparation of Authentic 11a and 11b. The Wittig reaction between methylthiomethylenetriphenylphosphorane (14.5 g, 0.04 mol) and *o*-phthalaldehyde (2.70 g, 0.02 mol) was carried out in THF at –75° for 8 hr to give a mixture of **11a** and **11b**, of ratio which was about 2:5 by nmr, in 50% (2.20 g) yield; nmr (C_6D_6) δ 1.80 (s, SMe), 1.86 (s, –SMe), 1.92 (s, –SMe), 5.92 and 6.55 (2xd, *J*=10.5 Hz, *cis* olefinic protons), 6.54 (s, *trans* olefinic protons), and 6.90–7.85 (m, 4H, aromatic protons).

Reactions of Vinylsulfonium Salts 8 and 12 with Sodium Phenoxide. The reactions were carried out in a similar manner. After similar treatment, the products, 9, and 13a and 13b, were obtained by distillation and recrystallization. Yields and some physical data of the products are shown in Table II.

Reaction of 3-Methylbutenyldimethylsulfonium Perchlorate (14) with Sodium Phenoxide. A mixture of **14** (6.10 g, 0.0265 mol) and sodium phenoxide (3.08 g, 0.0265 mol) in 100 ml of dry THF was refluxed for 14 hr. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel to give 2.60 g (42%) of crude 2-methyl-4-phenoxy-2-butene (**15**), which was distilled to afford the pure sample: bp 110° (18 mm); n_D^{20} 1.5957; ir (neat) 1660 (C=C) and 1230 cm^{-1} (C–O–Ph); mass spectrum (70 eV) *m/e* 162 (M^+); nmr (CCl_4) δ 1.72 and 1.77 (2xs, 6H, 2Me), 4.40 (d, 2H, *J*=7 Hz, CH_2OPh), 5.40 (t, 1H, *J*=7 Hz, olefinic proton) and 6.60–7.30 (m, 5H, aromatic protons).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.02 H, 8.78.

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6. All melting points of products were determined with a Yanagimoto micromelting apparatus and are uncorrected. The nmr spectra were obtained on a JEOL LNM-3H-60 spectrometer with tetramethylsilane as an internal standard. The ir spectra were recorded with a Jasco IR-E spectrometer. The mass spectra were taken with a Hitachi RMU-6E spectrometer.