Pergamon

Tetrahedron, Vol. 53, No. 30, pp. 10527-10544, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00665-0

Stereoselective Horner-Wittig Synthesis of (*Z*)-1-Chlorovinyl Sulfoxides[1].

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Abstract: This paper describes the synthesis of (*Z*)-1-chlorovinyl sulfoxides **1** by the Horner-Wittig reaction. The required [(α-chloro)sulfinylmethyl]diphenylphosphine oxides **2** (R^1=Me, *c*-Hex, Ph, *p*-Tol, *p*-(CF_3)Ph), were prepared in high yields by selective monochlorination and subsequent mono-oxidation of (thiomethyl)diphenylphosphine oxides **3**. The stable lithiated anions of **2** gave an efficient reaction with all structural types of aldehydes. Aromatic and α,β-unsaturated aldehydes gave **1** with excellent *Z*-selectivity (> 98%), irrespective of the nature of the substituent R^1 at sulfur. With straight chain aliphatic aldehydes, an aromatic substituent at sulfur was required to obtain high *Z*-selectivity. A mechanistic explanation for these observations is presented. An X-ray analysis of **1**, R^1=Me, R^2= 4-$MeOC_6H_4$ confirmed the *Z*-disposition of the chloro and aryl substituents.

INTRODUCTION

1-Chlorovinyl sulfoxides **1** form an only recently discovered class of multifunctional compounds that is expected to possess a versatile chemical reactivity, which is yet to be investigated (Michael additions, Diels-Alder reactions, [2+2]- and 1,3-dipolar cycloadditions). Two methods towards their synthesis have been described so far. Satoh *et al.*[2] reported the alkylation of an aldehyde by a lithiated chloromethyl sulfoxide, followed by mesitylation of the resulting α-hydroxy-β-chloro sulfoxide and subsequent DBU-assisted elimination of methanesulfonic acid. After the preparation of enantiomerically pure $(S)_C(S)_S$-(*O,O*-diethyl)-[(α-chloro)(*p*-tolylsulfinyl)methyl]phosphonate [$(EtO)_2P(O)CHClS(O)p$-Tol] by chlorination of the enantiomerically pure sulfoxide precursor with iodobenzene dichloride had been reported several years ago by Mikołajczyk *et al*[3], Kim *et al.*[4] and Mikołajczyk *et al*[5] very recently reported the synthesis of 1-chlorovinyl sulfoxides by the Horner-Wadsworth-Emmons reaction, using phosphonate carbanions. While the work of Kim et al. was restricted to aliphatic aldehydes, Mikołajczyk *et al* studied aldehydes of different structural types. Both the Satoh method and the HWE-reaction provide mixtures of *E*- and *Z*-isomers. The chemical potential of this new class of bis-heterosubstituted olefins incited us to develop a new route towards their synthesis by the Horner-Wittig reaction. Based upon previous experience by us and by others[6], we anticipated to obtain these 1-chlorovinyl sulfoxides with high stereoselectivity, when performing the Horner-Wittig protocol with appropriately substituted methyldiphenylphosphine oxides. Our preliminary experiments confirmed this assumption[1]. The required [(α-chloro)sulfinylmethyl]diphenyl- phosphine oxides **2** were found to be readily accessible by selective

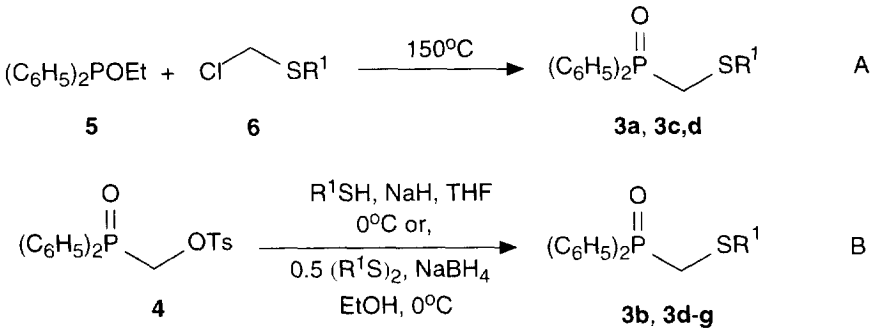
monochlorination and mono-oxidation of (thiomethyl)diphenylphosphine oxides **3**. We have developed a more general synthesis of the latter, involving nucleophilic substitution of (tosyloxymethyl)diphenylphosphine oxide **4**[7] with sulfur nucleophiles.

No examples of Horner-Wittig reactions of metallated α-halo-substituted phosphine oxides are known at present. It was anticipated, however, that the excellent anion-stabilizing properties of the diphenylphosphinoyl group would prevent α-elimination of lithium chloride from the lithiated anions of **2**, the actual reacting species.

RESULTS

Synthesis of (thiomethyl)diphenylphosphine oxides

Two different routes for the preparation of (thiomethyl)diphenylphosphine oxides **3** have been elaborated (Scheme 1). Arbuzov reaction of (*O*-ethyl)diphenylphosphinite **5** with an appropriate (chloromethyl)thioether **6**[8], according to a literature procedure[9], gave phosphine oxides **3a**, R^1=Me, **3c**, R^1=Ph and **3d**, R^1=*p*-Tol in high yields, after purification by crystallization from ethyl acetate (Table 1, method A). The synthesis of phosphine oxides **3** by this route is restricted by the limited availability of (chloromethyl)thioethers **6**. Therefore, it was decided to develop a more general procedure. Nucleophilic displacement at (tosyloxymethyl)diphenylphosphine oxide **4**[7] with sulfur nucleophiles (Scheme 1, method B) gave access to a wide range of substituents R^1 in **3**. The sulfur nucleophiles R^1SNa could either be prepared *in situ* by deprotonation of readily available thiols (R^1=*p*-Tol, *n*-Bu, *t*-Bu) or by reductive cleavage of a disulfide (R^1= *p*-(CF_3)Ph)[10]. Extractive work-up afforded phosphine oxides **3b** and **3d-g**, sufficiently pure for further elaboration. As shown in Table 1, method B gave almost quantitative yields throughout.



Scheme 1. Synthesis of (Thiomethyl)diphenylphosphine Oxides.

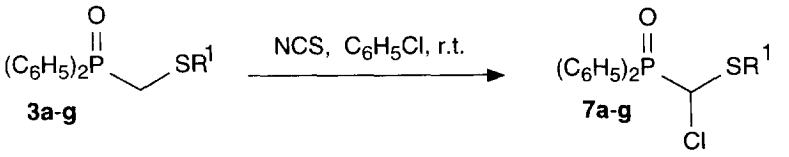
Synthesis of [(α-chloro)thiomethyl]diphenylphosphine oxides

The α-protons of aliphatic thioethers are susceptible to substitution by chlorine by the action of *N*-chlorosuccinimide (NCS)[11]. Warren *et al.* studied the chlorination of α-phenylthioalkyl- and α-methylthioalkyl-diphenylphosphine oxides (NCS, CCl_4, 50 °C) and obtained mixtures of mono- and di-chlorinated products[12]. Treatment of phosphine oxides **3a-g** with one equivalent of NCS in dry chlorobenzene at room temperature resulted in selective formation of the desired [(α-chloro)thiomethyl]diphenylphosphine oxides

7a-g (Scheme 2).

Table 1. Yields of (Thiomethyl)diphenylphosphine Oxides **3a-g**.

Compound	R^1	Method	Yield (%)
3a	methyl	A	80
3b	*c*-hexyl	B	95
3c	phenyl	A	85
3d	*p*-tolyl	A	98
		B	96
3e	*p*-(trifluoromethyl)phenyl	B	83
3f	*t*-butyl	B	98
3g	*n*-butyl	B	95



Scheme 2. Synthesis of [(α-Chloro)thiomethyl]diphenylphosphine Oxides.

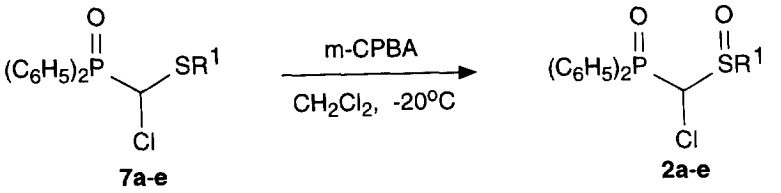
The concomitantly formed succinimide was easily removed by repeated extraction with water. Phosphine oxides **7a-g** were isolated in high yields after drying and evaporation of the solvent (Table 2). The products were sufficiently pure for further use.

Table 2. Yields of [(α-Chloro)thiomethyl]diphenylphosphine Oxides **7a-g**.

Compound	R^1	Yield (%)
7a	methyl	95
7b	*c*-hexyl	83
7c	phenyl	89
7d	*p*-tolyl	98
7e	*p*-(trifluoromethyl)phenyl	76
7f	*t*-butyl	80
7g	*n*-butyl	95

Synthesis of [(α-chloro)sulfinylmethyl]diphenylphosphine oxides

Selective mono-oxidation of phosphine oxides **7a,b** with one equivalent of *m*-CPBA proceeded cleanly at −20°C in CH_2Cl_2 (Scheme 3)[13]. Extractive work-up yielded the pure sulfoxides **2a** and **2b** in excellent yields (Table 3). No further purification of these phosphine oxides was necessary for subsequent use in the Horner-Wittig reaction. Treatment of *S*-aryl substituted phosphine oxides **7c** and **7d** with *one* equivalent of *m*-CPBA led to almost complete conversion (> 95%) of the starting material. As evidenced by ^{1}H-NMR analysis of the crude products, some overoxidation of the aryl-substituted sulfur center of sulfoxides **2c** and **2d** to the corresponding sulfones had occurred (<5%).



7a-e **2a-e**

Scheme 3. Synthesis of [(α-Chloro)sulfinylmethyl]diphenylphosphine Oxides.

Phosphine oxides **2c-e** and **2d** could be obtained pure by repeated crystallization from THF. This however, resulted in considerable loss of material. As will be shown below, the use of crude phosphine oxides **2c-e** in the Horner-Wittig reaction did not hamper the isolation of pure 1-chlorovinyl sulfoxides **1**, R^1=aryl. Oxidation of *S*-*t*-butyl substituted phosphine oxide **7f** proceeded less satisfactorily. After several hours at room temperature, only partial oxidation of this sterically shielded sulfide was observed. Exploitation of this phosphine oxide was therefore not further investigated. The preparation of phosphine oxide **2e**, carrying a strongly electron withdrawing substituent at sulfur, was of particular interest to us, because the 1-chlorovinyl sulfoxides derived from it are expected to show an enhanced reactivity in Michael-type and cycloaddition reactions.

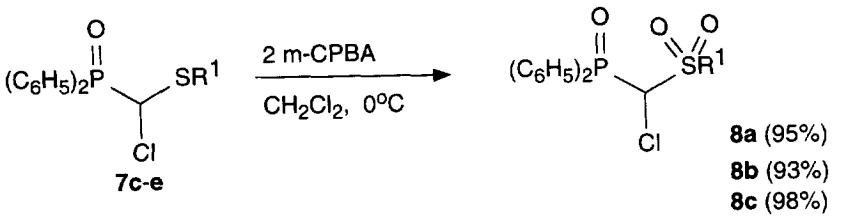
Table 3. Yields of [(α-Chloro)sulfinylmethyl]diphenylphosphine Oxides **2a-d**.

Compound	R^1	Yield (%)
2a	methyl	93
2b	c-hexyl	97
2c	phenyl	97
2d	*p*-tolyl	98
2e	*p*-(trifluoromethyl)phenyl	97

The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra of phosphine oxides **2a-e** showed well-separated signals for both possible diastereomers. The diastereomeric ratio varied between oxidation experiments. This may be

caused by epimerization at the central carbon atom of **2** during the basic aqueous conditions required to remove the side product of the oxidation: *m*-chlorobenzoic acid[3].

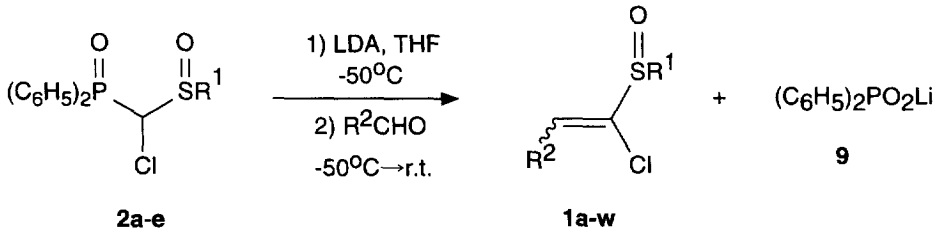
[(α-Chloro)(arylsulfonyl)methyl]diphenylphosphine oxides **8c-e** were easily prepared in almost quantitative yield by oxidation of phosphine oxides **7c-e** with two equivalents of *m*-CPBA (Scheme 4).



Scheme 4. Synthesis of [(α-Chloro)(arylsulfonyl)methyl]diphenylphosphine Oxides.

Horner-Wittig synthesis of 1-chlorovinyl sulfoxides

Phosphine oxides **2a-d** were readily deprotonated by LDA in THF at −50°C to give intensely yellow-colored solutions of the anions. Deprotonation at lower temperatures was hampered by insufficient solubility of the phosphine oxides. The lithiated phosphine oxides **2**-Li proved sufficiently stable to allow an efficient reaction with a broad range of aldehydes (R^2CHO). The Horner-Wittig reaction was readily completed by allowing the reaction mixture to warm to room temperature, as evidenced by the white precipitate (lithium diphenylphosphinate **9**) that gradually formed (Scheme 5). Extractive work-up, followed by column chromatography, afforded the analytically pure 1-chlorovinyl sulfoxides **1a-w** in good yields throughout (Table 4).



Scheme 5. Horner-Wittig Synthesis of 1-Chlorovinyl Sulfoxides.

In most cases, the formation of 1-chlorovinyl sulfoxides **1** proceeded with excellent stereoselectivity. With aromatic aldehydes and α,β-unsaturated aldehydes, almost exclusive formation of one stereoisomer was observed, regardless of the substituent at sulfur (Table 4, entries **1a-f**, **1k** and **1p-s**). A crystal structure determination of 1-chlorovinyl sulfoxide **1c**, derived from phosphine oxide **2a** (R^1=Me) and anisaldehyde (4-$MeOC_6H_4CHO$), revealed the thermodynamically favored *Z*-geometry around the newly formed double bond (see below). The stereoselectivity of the reaction with straight chain aliphatic

Table 4. Yields and *Z*:*E* ratios of 1-Chlorovinyl Sulfoxides **1a-w**.

Compound	R^1	R^2	Yield (%)	*Z*:*E*
1a	methyl	phenyl	75	>98:2[a]
1b	methyl	4-chlorophenyl	70	>98:2[a]
1c	methyl	4-methoxyphenyl	71	>98:2[a]
1d	methyl	2-thienyl	60	>98:2[a]
1e	methyl	1-butenyl	59	>98:2[a]
1f	methyl	phenylethenyl	87	>98:2[a]
1g	methyl	*n*-butyl	63[e]	4.7:1[b]
1h	methyl	*c*-hexyl	68[e]	3.0:1[b]
1i	*c*-hexyl	*n*-butyl	56[e]	5.2:1[b]
1j	phenyl	H	72	-
1k	phenyl	1-propenyl	63	97:3[c]
1l	phenyl	methyl	71	92:8[c]
1m	phenyl	*n*-propyl	70	97:3[c]
1n	phenyl	*n*-butyl	63	96:4[c]
1o	*p*-tolyl	H	72	-
1p	*p*-tolyl	phenyl	60	>98:2[a]
1q	*p*-tolyl	4-methoxyphenyl	66	>98:2[a]
1r	*p*-tolyl	4-(methyl-thio)phenyl	63	>98:2[a]
1s	*p*-tolyl	1-propenyl	71	96:4[c]
1t	*p*-tolyl	*n*-butyl	74	96:4[c]
1u	*p*-tolyl	*c*-hexyl	69	3.3:1[d]
1v	*p*-(trifluoromethyl)phenyl	H	75	-
1w	*p*-(trifluoromethyl)phenyl	*n*-propyl	67	>98:2[a]

[a] Only one isomer observed by ^{1}H- and ^{13}C-NMR. [b] *Z*/*E* ratio determined by ^{1}H-NMR of the crude product corresponds well with the yields of the separated isomers. [c] *Z*/*E* ratio determined by gas chromatography. [d] *Z*/*E* ratio determined by ^{1}H-NMR of the purified product. [e] Total yield of the separated *Z*- and *E*-isomers.

aldehydes was found to depend strongly on the substituent at sulfur in the Horner-Wittig reagent **2**. In the case of R^1=Me (**2a**) and R^1=*c*-Hex (**2b**), only a modest stereoselectivity was observed (Table 4, entries **1g** and **1i**). The two geometric isomers of these 1-chlorovinyl sulfoxides were obtained pure after separation by column chromatography. The stereoselectivity could be greatly improved by changing the substituent at sulfur. Reaction with **2c**-Li, **2d**-Li and **2e**-Li, possessing an aromatic substituent R^1 at sulfur, showed again a strong preference for formation of one geometric isomer (Table 4, entries **1l-n**, **1t**, **1w**). Surprisingly, in the case of the sterically more hindered cyclohexanecarboxaldehyde, the stereoselectivity hardly improved upon changing the substituent R^1 at sulfur from Me to *p*-Tol (Table 4, entries **1h** and **1u**). In the case of **1h**, the *Z*- and *E*-isomers could be separated by column chromatography. In analogy with what was shown to be the case for **1c**, it is assumed that in all cases described above, the thermodynamically more stable *Z*-isomer is the one predominantly or exclusively formed. The preparation of 1-chlorovinyl sulfoxides **1j**, **1o** and **1v**, the simplest members of this class of compounds, by a Horner-Wittig reaction with carefully dried paraformaldehyde[14], was given special attention. These compounds are the substrates of choice for a first investigation of the reactivity of 1-chlorovinyl sulfoxides.

Lithiated phosphine oxide **2a** failed to react with ketones (cyclohexanone and benzophenone). Upon work-up, only starting material was recovered. This lack of reactivity is ascribed to the bulkiness of the tri-substituted carbanion **2a**-Li. A similar observation was made for sterically hindered pivaldehyde. Attempted Horner-Wittig reactions of **2a** with ketones, using $KN(SiMe_3)_2$ as the base, were not successful.

1-Chlorovinyl sulfide **10** was obtained from phosphine oxide **7c** and butanal in 77% yield, as a mixture of geometric isomers in a ratio of approximately 3:1 (^{13}C-NMR). A Horner-Wittig reaction of phosphine oxide **8c** with butanal afforded stereochemically pure (*Z*)-1-chlorovinyl sulfone **11** in 64% yield[15].

As mentioned earlier, sulfinyl-substituted phosphine oxides **2c-e** contained small amounts of α-chlorosulfides **7c-e**, as well as of α-chlorosulfones **8c-e**. Nevertheless, these phosphine oxides can be successfully applied in the Horner-Wittig reaction. When using the crude phosphine oxide **2c** in a Horner-Wittig reaction with butanal, the 1-chlorovinyl sulfoxide **1m** was shown to be contaminated with small amounts of 1-chlorovinyl sulfide **10** and 1-chlorovinyl sulfone **11**. These impurities, however, could be easily removed by column chromatography. In fact, all 1-chlorovinyl sulfoxides **1**, with R^1=aryl described here, were easily obtained pure in the yields indicated in Table 4. A Horner-Wittig reaction of lithiated phosphine oxide **8c** with formaldehyde was also successful. The resulting 1-chlorovinyl sulfone **12**, obtained in 73% yield, is known to be a good reaction partner, both in Diels-Alder and in 1,3-dipolar cycloaddition reactions[16].

Crystal structure of (Z)-1-[2-chloro-2-(methylsulfinyl)ethenyl]-4-methoxybenzene

The structure of 1-chlorovinyl sulfoxide **1c**, with R^1=Me and R^2=4-$MeOC_6H_4$ was determined by X-ray analysis. A suitable colorless crystal was obtained by crystallization from toluene. Figure 1 shows an ORTEP projection of **1c**, together with the adopted numbering scheme.

The unit cell of **1c** contains two pairs of both enantiomers. The *S*-enantiomers of these pairs, presented in Figure 1, were found to have slightly different spatial arrangements and different bond lengths (this, of course, also holds for the two *R*-enantiomers). This is probably a result of crystal packing forces. In the experimental part, selected bond lengths, bond angles and dihedral angles of both *S*-enantiomers are listed. The X-ray structure clearly establishes the sterically less hindered *Z*-configuration for 1-chlorovinyl

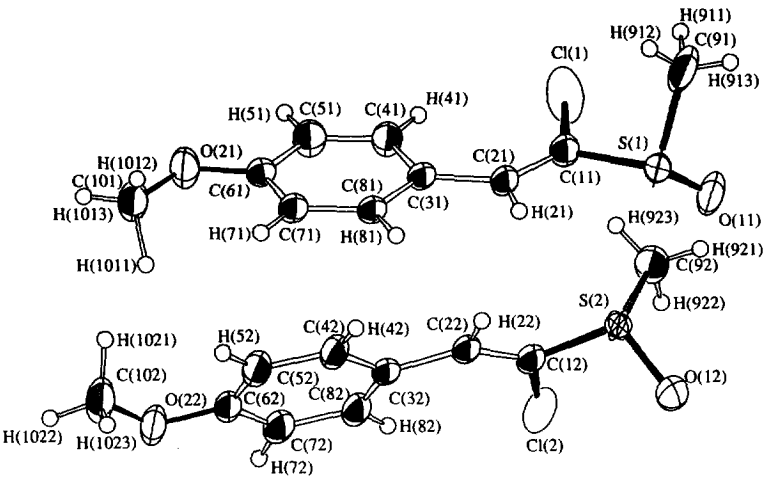


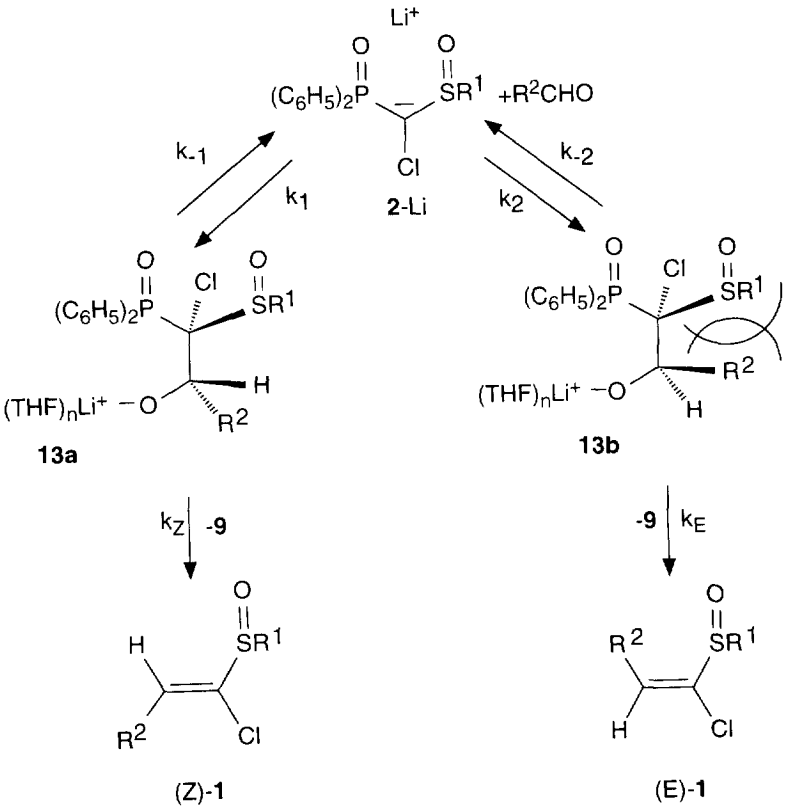
Figure 1. Crystal structure of **1c**.

sulfoxide **1c**; *i.e.*: the 4-methoxyphenyl substituent and the chlorine atom are positioned at the same side of the double bond. Furthermore, the 4-methoxyphenyl ring practically lies in one plane with the C=C double bond. The C_1-C_2-C_3-C_4 dihedral angles are 5(1)° and 2.1(4)° for the two individual *S*-enantiomers, respectively. This indicates the presence of strong conjugation between the 4-methoxy substituted aromatic ring and the strongly electrophilic, sulfinyl-and-chlorine substituted, olefinic bond. The tetrahedral geometry of the sulfur center is distorted[17]. Repulsion between the free electron pair at sulfur and the $S^{\delta+}$-$O^{\delta-}$ bond compresses the angle between the two S-C bonds; bond angles of 98.2(3) and 99.8(3)° were found for the two *S*-enantiomers.

MECHANISTIC CONSIDERATIONS

The mechanism of the Horner-Wittig reaction[6,18], leading to the formation of 1-chlorovinyl sulfoxides **1**, is depicted in Scheme 6. The lithiated phosphine oxide anions **2**-Li react rapidly at low temperatures (k_1 and k_2 are large) with the aldehyde (R^2CHO) to give a mixture of two diastereomeric Horner-Wittig adducts **13a** (pro-*Z*) and **13b** (pro-*E*). Subsequently, these lithiated Horner-Wittig adducts decompose by elimination of lithium diphenylphosphinate **9** to the (*Z*)- and (*E*)-isomers of 1-chlorovinyl sulfoxides **1**. The decomposition of the intermediate Horner-Wittig adducts probably proceeds via an oxaphosphetane intermediate[19]. The preferred formation of (*Z*)-1-chlorovinyl sulfoxides (*Z*)-**1** can be rationalized by assuming a fast equilibrium between the two Horner-Wittig adducts **13a** and **13b**[20]. This

equilibrium is established by reverse reactions (k_{-1} and k_{-2}) of these adducts to their common constituting phosphine oxide anion **2**-Li and the aldehyde R^2CHO. In order to obtain the observed pronounced *Z*-selectivity, according to the Curtin-Hammett Principle, a second kinetic condition must be met. The rate of decomposition of the pro-*Z* adduct **13a** into 1-chlorovinyl sulfoxide (*Z*)-**1** needs to be much faster compared with its pro-*E* congener **13b** (thus, $k_Z >> k_E$)[20]. This condition is fulfilled because steric repulsion builds up in **13b** between the sulfinyl substituent [$S(O)R^1$] and R^2 during rotation around the newly formed carbon-carbon bond to reach the eclipsed conformation, depicted in Scheme 6, necessary for completion of the Horner-Wittig reaction. In the eclipsed conformation of pro-*Z* adduct **13a**, substituent R^2 opposes the smaller chlorine atom.



Scheme 6. Mechanism of the Horner-Wittig reaction.

When straight chain aliphatic aldehydes were used as substrates in the Horner-Wittig reaction with **2**-Li, the presence of an aromatic sulfur substituent (R^1) in the phosphine oxide proved to be a necessary condition in order to obtain the *Z*-isomer of **1** with high stereoselectivity. As outlined above, a fast

reversal of the Horner-Wittig adducts **13a** and **13b** into **2**-Li and aldehyde is a prerequisite for good selectivity. The energy barrier for the reverse reaction is lowered, and k_{-1} and k_{-2} increase, if the developing negative charge at the central carbon atom of phosphine oxide **2** is better stabilized during the process of carbon-carbon bond breaking. Replacement of an electron-donating alkyl substituent at sulfur by an aromatic substituent in phosphine oxides **2** will impart additional stabilization to the sulfinyl-substituted phosphine oxide anions **2**-Li. This well explains the highly improved *Z*-selectivity which is observed in the Horner-Wittig reaction of **2c**-Li with straight chain aliphatic aldehydes. Conjugation within the re-formed aldehyde will also facilitate the reverse reactions. This is undoubtedly the reason that in the case of aromatic aldehydes and α,β-unsaturated aldehydes, an excellent *Z*-selectivity is observed, irrespective of the nature of the substituent R^1 at sulfur in phosphine oxide **2**.

CONCLUDING REMARKS

The lithiated anions of [(α-chloro)sulfinylmethyl]diphenylphosphine oxides **2a-e** are sufficiently stable at low temperatures to allow an efficient Horner-Wittig reaction with all structural types of aldehydes. 1-Chlorovinyl sulfoxides **1** can be isolated in good yields. Horner-Wittig reaction of **2** with aromatic aldehydes and α,β-unsaturated aldehydes gave 1-chlorovinyl sulfoxides **1** with excellent *Z*-selectivity (>98%), irrespective of the nature of the substituent R^1 at sulfur. In order to obtain a high *Z*-selectivity with straight chain aliphatic aldehydes, an aromatic sulfur substituent R^1 in phosphine oxide **2** was required. X-ray analysis of 1-[2-chloro-2-(methylsulfinyl)ethenyl]-4-methoxybenzene (**1c**), the only isomer formed by the the reaction of **2a**-Li and anisaldehyde, showed this compound to possess the *Z*-configuration.

The reactivity of 1-chlorovinyl sulfoxides in Michael-type as well as in cycloaddition reactions is presently under investigation.

EXPERIMENTAL

THF (from $LiAlH_4$), CH_2Cl_2 (from CaH_2), chlorobenzene (from P_2O_5), EtOAc and petroleum ether (40/60) were distilled before use. Column chromatography was performed using Merck Kieselgel 60 (0.0040-0.0063 mm). TLC analyses were performed on Schleicher and Schuell F1500/LS 254 silica plates, using UV detection or a spray of $KMnO_4$ in acetone. ^1H- (200 MHz), ^{13}C- (50 MHz) and ^{31}P- (80 MHz) NMR spectra were recorded on a Jeol NM FX-200 spectrometer using deuterochloroform as the solvent. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (TMS) or 85% phosphoric acid. Coupling constants (J) are given in Hz. Melting points were determined on a Büchi melting point apparatus and are uncorrected. A CP-Sil-19CB column (length: 25m, inside diameter: 0.22 mm) was used for the gas chromatographic experiments. Elemental analyses were performed at the Microanalytical Laboratory, Department of Chemistry, University College Dublin, Ireland.

[(c-Hexylthio)methyl]diphenylphosphine oxide (3b). A 250 ml three-necked round-bottomed flask was charged with 0.8 g of a 60% NaH suspension in mineral oil (0.48 g, 20 mmol) under a nitrogen atmosphere. The NaH was washed three times with 10 ml of petroleum ether (40/60) and suspended in 50 ml of dry THF. To this suspension, a solution of

2.44 ml (20 mmol) of cyclohexyl mercaptan in 25 ml of THF was added over a period of 0.5 h at 0°C. After stirring for 1 h at room temperature, 5.79 g of solid tosylate **4** was added in two portions and an exothermic reaction ensued. After stirring overnight, the reaction mixture was poured into 250 ml of saturated K_2CO_3. The THF layer was separated and the water layer was extracted two times with 100 ml of CH_2Cl_2. The combined organic layers were extracted three times with 100 ml of demineralized water, dried on $MgSO_4$ and evaporated *in vacuo*. The crude phosphine oxide (6.27, 95%) was sufficiently pure for further elaboration. An analytical sample was obtained by a crystallization from EtOAc. ^{1}H-NMR: δ 1.08-1.24 (m, 6H, $(CH_2)_3$); 1.60-1.84 (m, 2H, CH_2); 1.84-2.12 (m, 2H, CH_2); 2.60-2.84 (m, 1H, CH); 3.28 (d, J_{PH}=9.2, 2H, PCH_2); 7.40-7.68 (m, 6H); 7.76-8.00 (m, 4H). ^{13}C-NMR: δ 25.49, 25.70, 32.85 (CH_2); 28.18 (d, J_{PC}=70.4, P-C). ^{31}P-NMR: δ 30.46. Anal. cald. for $C_{19}H_{23}POS$ (330.42): C 69.07 H 7.02; found: C 69.09 H 7.13. M.p. 121-3°C.

[(*p*-Tolylthio)methyl]diphenylphosphine oxide (**3d**). Phosphine oxide **3d** was prepared according to the above procedure using *p*-thiocresol. ^{1}H-NMR: δ 2.28 (s, 3H, CH_3); 3.69 (d, J_{PH}=9.3, 2H, PCH_2); 7.01 (d, J=8.2, 2H); 7.21 (d, J=8.2, 2H); 7.36-7.60 (m, 6H); 7.68-7.88 (m, 4H). ^{13}C-NMR: δ 20.88 (CH_3); 34.44 (d, J_{PC}=69, P-C). ^{31}P-NMR: δ 28.84. M.p. 99-101°C.

[(*t*-Butylthio)methyl]diphenylphosphine oxide (**3f**). Phosphine oxide **3f** was prepared according to the above procedure using the commercially available sodium salt of 2-methyl-2-propanethiol (Aldrich). ^{1}H-NMR: δ 1.27 (s, 9H, $(CH_3)_3$); 3.30 (d, J_{PC}=12.3, 2H, P-CH_2); 7.36-7.60 (m, 6H); 7.68-7.88 (m, 4H). ^{13}C-NMR: δ 20.90 (($CH_3)_3$); 27.24 (d, J_{PC}=69, P-C); 43.15 (d, J=5.9, C-*t*-Bu). ^{31}P-NMR: δ 30.07. Anal. cald. for $C_{17}H_{21}OPS$ (304.38): C 67.08 H 6.95; found: C 67.05 H 6.96. M.p. 155-7°C.

[(*n*-Butylthio)methyl]diphenylphosphine oxide (**3g**). Phosphine oxide **3g** was prepared according to the above procedure using *n*-butanethiol. ^{1}H-NMR: δ 0.85 (t, J=7.7, 3H, CH_3); 1.16-1.40 (m, 2H, CH_2), 1.40-1.60 (m, 2H, CH_2); 2.61 (t, J=7.2, 2H, SCH_2); 3.25 (d, J_{PH}=8.8, 2H, P-CH_2); 7.36-7.64 (m, 6H); 7.72-7.88 (m, 4H). ^{13}C-NMR: δ 13.4 (CH_3); 21.5 (CH_2); 29.9 (d, J_{PC}=70, P-C); 30.9 (SCH_2); 33.7 (CH_2). ^{31}P-NMR: δ 29.8. Anal. cald. for $C_{17}H_{21}OPS$ (304.39): C 67.08 H 6.95; found: C 67.37 H 6.94. M.p. 109-111°C.

[*p*-((Trifluoromethyl)phenylthio)methyl]diphenylphosphine oxide (**3e**). A 250 ml, three-necked, round-bottomed, flask was charged with 7.12 g (20.1 mmol) di-*p*-(trifluoromethyl)phenyldisulfide and 100 ml of absolute ethanol. The solution was purged with nitrogen for 30 min. At 0 C, 1.7 g (47 mmol) of $NaBH_4$ was added in small portions (Caution ! Reduction of the disulfide is exothermic and vigorous hydrogen evolution occurs). Subsequently, the solid phosphine oxide **4** (16.15 g, 42 mmol) was added to the reaction mixture in two equal portions. The reaction vessel was sealed and stirring was continued overnight at room temperature. The reaction mixture was poured into 80 ml of saturated K_2CO_3 and extracted three times with 100 ml of CH_2Cl_2. The combined organic layers were extracted two times with 50 ml of saturated K_2CO_3 and 80 ml of saturated brine. Subsequent drying on $MgSO_4$ and evaporation of the solvent *in vacuo* gave the crude phosphine oxide **3e** as a white solid of which 12.16 g (33.7 mmol, 83%) was obtained pure by crystallization from ethyl acetate/ petroleum ether (40/60). ^{1}H-NMR: δ 3.74 (d, J_{PH}=8.7, 2H, PCH); 7.36-7.60 (m, 10H); 7.72-7.84 (m, 4H). ^{13}C-NMR: δ 32.5 (d, J_{PC}=67.4, P-C). ^{31}P-NMR: δ 28.19. M.p. 108-9 C.

[(α-Chloro)(methylthio)methyl]diphenylphosphine oxide (**7a**). A one liter round-bottomed flask was charged with 400 ml of dry chlorobenzene and 10.48 g (40 mmol) of the starting phosphine oxide **3a** was dissolved by heating the chlorobenzene to 50°C. The resulting colorless clear solution was allowed to cool to room temperature (**3a** recrystallized if its concentration exceeded 0.1 M). *N*-Chlorosuccinimide (NCS), 5.61 g (42 mmol), was added in six portions over a period of 1 h. A white precipitate (succinimide) usually appeared after half of the NCS had been added. After stirring overnight, the reaction mixture was extracted three times with 300 ml of demineralized water and dried with $MgSO_4$. The chlorobenzene was evaporated *in vacuo* leaving 11.07 g (38 mmol, 95 %) of **7a** as a white solid. The crude product was sufficiently pure for further elaboration. An analytical sample was obtained by a crystallization from CH_2Cl_2/petroleum ether (40/60). ^{1}H-NMR: δ 2.41 (s, 3H, SCH_3); 5.52 (d, J_{PH}=5.6, 1H, P-CH); 7.36-7.60 (m, 6H); 7.76-

8.00 (m, 4H). ^{13}C-NMR: δ 15.2 (SCH_3); 62.4 (d, J_{PC}=72, P-C). ^{31}P-NMR: δ 30.8. Anal. cald. for $C_{14}H_{14}ClOPS$ (296.75): C 56.66 H 4.76; found: C 56.44 H 4.74. M.p. 179-180°C.

[(α-Chloro)(*c*-hexylthio)methyl]diphenylphosphine oxide (7b). Phosphine oxide **7b** was prepared according to the above procedure using **3b**. ^{1}H-NMR: δ 1.08-1.28 (m, 5H, CH_2); 1.28-1.85 (m, 3H, CH_2); 1.84-2.08 (m, 2H, CH_2); 2.96-3.16 (m, 1H, S-CH); 5.66 (d, J_{PH}=9.8, 1H, P-CH); 7.16-7.68 (m, 6H); 7.76-8.08 (m, 4H). ^{13}C-NMR: δ 25.43, 25.52, 25.78, 32.71, 32.82 (CH_2); 45.89 (d, J_{PC}=4.4, S-C); 60.17 (d, J_{PC}=62, P-C). ^{31}P-NMR: δ 30.71. Anal. cald. for $C_{19}H_{22}ClOPS$ (364.87): C 62.55 H 6.08; found: C 62.54 H 6.04. M.p. 196-8°C.

[(α-Chloro)(phenylthio)methyl]diphenylphosphine oxide (7c). Phosphine oxide **7c** was prepared according to the above procedure using **3c**. In this case, last traces of chlorobenzene could only be removed by stirring the crude product in diethyl ether. ^{1}H-NMR: δ 5.72 (d, J_{PH}=8.2, 1H, P-CH); 7.20-7.40 (m, 3H); 7.40-7.72 (m, 8H); 7.80-8.08 (m, 4H). ^{13}C-NMR: δ 65.70 (d, J_{PC}=67, P-CH). ^{31}P-NMR: δ 30.43. M.p. 169-170°C.

[(α-Chloro)(*p*-tolylthio)methyl]diphenylphosphine oxide (7d). Phosphine oxide **7d** was prepared according to the above procedure using **3d**. In this case, last traces of chlorobenzene could only be removed by stirring the crude product in diethyl ether. ^{1}H-NMR: δ 2.34 (s, 3H, CH_3); 5.65 (d, J_{PH}=7.7, 1H, P-CH); 7.13 (d, J=8.2, 2H); 7.39 (d, J=8.2, 2H); 7.40-7.72 (m, 6H); 7.80-8.12 (m, 4H). ^{13}C-NMR: δ 21.06 (CH_3); 66.26 (d, J_{PC}=67, P-C). ^{31}P-NMR: δ 30.38. Anal. cald. for $C_{20}H_{18}ClOPS$ (372.85): C 64.43 H 4.87; found: 64.26 H 4.86. M.p. 180-5°C.

[(α-Chloro)((*p*-trifluoromethyl)phenylthio)methyl]diphenylphosphine oxide (7e). Phosphine oxide **7e** was prepared according to the above procedure using **3e**. ^{1}H-NMR: δ 5.76 (d, J_{PH}=8.2, 1H, P-CH); 7.51-7.66 (m, 10H); 7.83-8.08 (m, 4H). ^{13}C-NMR: δ 63.9 (d, J_{PC}=66, P-C). ^{31}P-NMR: δ 40.42. M.p. 179-180 C.

[(α-Chloro)(*t*-butylthio)methyl]diphenylphosphine oxide (7f). Phosphine oxide **7f** was prepared according to the above procedure using **3f**. ^{1}H-NMR: δ 1.33 (s, 9H, $(CH_3)_3$); 5.58 (d, J_{PH}=8.3, 1H, P-CH); 7.36-7.64 (m, 6H); 7.80-8.08 (m, 4H). ^{13}C-NMR: δ 30.43 (CH_3); 46.95 (d, J_{PC}=5.9, S-C); 59.89 (d, J_{PC}=73, P-C). ^{31}P-NMR: δ 31.17. Anal. cald. for $C_{17}H_{20}ClOPS$ (338.83): C 60.26 H 5.95; found: C 60.05 H 5.87. M.p. 203-6°C.

[(α-Chloro)(*n*-butylthio)methyl]diphenylphosphine oxide (7g). Phosphine oxide **7g** was prepared according to the above procedure using **3g**. ^{1}H-NMR: δ 0.88 (t, J=7.2, 3H, CH_3); 1.24-1.44 (m, 2H, CH_2); 1.48-1.68 (m, 2H, CH_2); 2.88 (t, J=6.8, 2H, SCH_2); 5.57 (d, J_{PH}=7.2, 1H, P-CH); 7.40-7.64 (m, 6H); 7.80-8.04 (m, 4H). ^{13}C-NMR: δ 13.4 (CH_3); 21.6 (CH_2); 30.4, 32.6 (CH_2, SCH_2); 61.1 (d, J_{PC}=70, P-C). ^{31}P-NMR: δ 30.7. Anal. cald. for $C_{17}H_{20}ClOPS$ (338.83): C 60.26 H 5.95; found: C 60.10 H 5.97. M.p. 161-2°C.

[(α-Chloro)(methylsulfinyl)methyl]diphenylphosphine oxide (2a). A solution of 5.93 g (20 mmol) of phosphine oxide **7a** in 150 ml of CH_2Cl_2 was cooled to −20°C. Over a period of 1 h, 4.93 g crude *m*-CPBA (Janssen, 70% purity, containing 20 mmol of the oxidizing agent) was added. A white precipitate gradually formed. The oxidation was monitored by TLC (EtOAc). After completion of the reaction, which took about 1 h, an extra 100 ml of CH_2Cl_2 was added. The colorless clear solution was extracted three times with 100 ml of sat K_2CO_3. Complete removal of the concomitantly formed *m*-chlorobenzoic acid was checked by TLC (EtOAc). The organic layer was dried overnight with $MgSO_4$. Evaporation of the solvent *in vacuo* gave 5.81 g (93%) of a white solid. The isolated phosphine oxide **2a** was sufficiently pure for further application in a Horner-Wittig reaction. An analytical sample was obtained by crystallization from CH_2Cl_2/petroleum ether (40/60). ^{1}H-NMR: δ 2.88, 2.89 (2xs, $S(O)CH_3$); 5.10 (d, J_{PH}=8.2, P-CH); 5.66 (d, J_{PC}=3.6, P-CH); 7.40-7.72 (m, 6H), 7.80-8.04 (m, 4H). ^{13}C-NMR: δ 35.48, 38.00 ($S(O)CH_3$); 69.99 (d, J_{PC}=61, P-C); 70.40 (d, J_{PC}=55, P-C). ^{31}P-NMR: δ 24.31, 31.11. Anal. cald. for $C_{14}H_{14}ClO_2PS$ (312.75): C 53.77 H 4.51; found: C 53.67 H 4.51.

[(α-Chloro)(*c*-hexylsulfinyl)methyl]diphenylphosphine oxide (2b). Phosphine oxide **2a** was prepared according to the above procedure using **7b**. Complete oxidation required about 1 h. ^{1}H-NMR: δ 1.04-2.08 (m, $(CH_2)_5$); 3.00-3.10, 3.10-3.36 (2xm, S-CH); 5.11 (d, J_{PH}=9.3, P-CH); 5.32 (d, J_{PH}=2.5, P-CH); 7.24-7.72 (m, 6H); 7.80-8.08 (m, 4H). ^{13}C-NMR: δ 66.63 (d, J_{PC}=64, P-C); 65.90 (d, J_{PC}=59, P-C). ^{31}P-NMR: δ 27.33, 31.61. Anal. Cald. for $C_{19}H_{22}ClO_2PS$ (380.87): C 59.92 H 5.82; found: C 57.80 H 5.86. The low weight percentage of carbon may be explained by the presence of a very small amount of sulfone.

[(α-Chloro)(phenylsulfinyl)methyl]diphenylphosphine oxide (2c). The reaction mixture was allowed to stir for 48 h as the starting phosphine oxide **7c** showed only a modest solubility in cold CH_2Cl_2. The work-up procedure remained identical as described above. ^{1}H-NMR: δ 4.92 (d, J_{PH}=8.7, P-CH); 5.37 (d, J_{PH}=3.1, P-CH); 7.20-7.80 (m); 7.80-8.12 (m). ^{13}C-NMR: δ 71.38 (d, J_{PC}=57, P-C); 74.44 (d, J_{PC}=60, P-C). ^{31}P-NMR: δ 27.21, 31.89.

[(α-Chloro)(*p*-tolylsulfinyl)methyl]diphenylphosphine oxide (2d). The reaction mixture was allowed to stir for 48 h as the starting phosphine oxide **7d** showed only a modest solubility in cold CH_2Cl_2. The work-up procedure remained identical as described above. ^{1}H-NMR: δ 2.40 (s, CH_3); 4.88 (d, J_{PH}=8.7, P-CH); 5.34 (d, J_{PH}=3.1, P-CH); 7.20-7.36 (m); 7.40-7.72 (m); 7.76-8.08 (m). ^{13}C-NMR: δ 71.59 (d, J_{PC}=58, P-C); 74.79 (d, J_{PC}=60, P-C). ^{31}P-NMR: δ 26.73, 31.19.

[(α-Chloro)((*p*-(trifluoromethyl)phenylsulfinyl]diphenylphosphine oxide (2e). The reaction mixture was allowed to stir for 72 h as the starting phosphine oxide **7e** showed only a modest solubility in cold CH_2Cl_2. The work-up procedure remained identical as described above. ^{1}H-NMR: δ 4.91 (d, J_{PH}=8.2, P-CH); 5.43 (d, J_{PH}=4.1, P-CH); 7.43-7.98 (m). ^{13}C-NMR: δ 71.92 (d, J_{PC}=76, P-C); 74.14 (d, J_{PC}=58.6, P-C). ^{31}P-NMR: δ 26.43, 31.30

[(α-Chloro)(phenylsulfonyl)methyl]diphenylphosphine oxide (8c). Phosphine oxide **8c** was prepared by oxidation of sulfide **7c** with two equivalents of *m*-CPBA in CH_2Cl_2 at 0°C. The work-up procedure was identical as applied for the isolation of sulfoxide **2c**. ^{1}H-NMR: δ 5.52 (d, J_{PH}=6.2, 1H, P-CH); 7.36-7.72 (m, 6H); 7.80-8.08 (m, 4H). ^{13}C-NMR: δ 69.34 (d, J_{PC}=51, P-C); ^{31}P-NMR: δ 27.09. M.p. 210-5°C.

[(α-Chloro)(*p*-tolylsulfonyl)methyl]diphenylphosphine oxide (8d). Phosphine oxide **8d** was prepared by oxidation of sulfide **7d** with two equivalents of *m*-CPBA in CH_2Cl_2 at 0°C. The work-up procedure was identical as applied for the isolation of sulfoxide **2d**. ^{1}H-NMR: δ 2.43 (s, 3H, CH_3); 5.47 (d, J_{PH}=6.2, 1H, P-CH); 7.31 (d, J=8.2, 2H); 7.40-7.72 (m, 6H); 7.76-8.04 (m, 6H). ^{13}C-NMR: δ 21.76 (CH_3); 69.48 (d, J_{PC}=51, P-C). ^{31}P-NMR: δ 26.95. M.p. 215°C (dec).

[(α-Chloro)((*p*-(trifluoromethyl)phenylsulfonyl]diphenylphosphine oxide (8e). Phosphine oxide **8e** was prepared by oxidation of **7e** with 1.2 equivalents of *m*-CPBA in CH_2Cl_2. After addition of *m*-CPBA at −20°C, the mixture was allowed to reach room temperature and stirred overnight. The work-up procedure was identical as applied for the isolation of sulfoxide **2e**. ^{1}H-NMR: δ 5.47 (d, J_{PH}=5.1, 1H, P-CH); 7.91 (d, J_{HH}=8.2, 2H); 8.13 (d, J_{HH}=8.2, 2H); 7.49-7.94 (m, 10H). ^{13}C-NMR: δ 69.52 (d, J_{PC}=76, P-C). ^{31}P-NMR δ 26.52. M.p.: 208-212°C (dec).

General procedure for the Horner-Wittig synthesis of 1-chlorovinyl sulfoxides. A solution of 4 mmol of phosphine oxide **2a-d** in 40 ml of dry THF was cooled to −50°C. The starting phosphine oxide precipitated upon cooling. Aromatic aldehydes (4.4 mmol) were added to the reaction mixture prior to deprotonation. Over a period of 5 min, a solution of 4.1 mmol of lithium di-*iso*-propylamide, freshly prepared from 0.7 ml di-*iso*-propylamine (4.8 mmol) and 2.8 ml of a 1.6 M solution of *n*-BuLi (4.4 mmol) in hexanes in 10 ml of THF at −10°C, was added slowly to the reaction mixture in order to maintain the low temperature. After all solid material had dissolved into the yellow-colored reaction mixture, 4.4 mmol of the aldehyde, dissolved in 5 ml THF, was added within 1 min. For the synthesis of compounds **1i** and **1n**, carefully dried paraformaldehyde, 0.9 g (30 mmol) was added in five equal portions over a period of 15 min. The resulting colorless reaction mixture was allowed to slowly warm to room temperature and stirring was continued for 1-3 h. Between −20°C and 5°C, a white precipitate gradually formed. Subsequently, the reaction mixture was poured into 100 ml of demineralized water and extracted three times with 100 ml of diethyl ether. The combined organic layers were dried with $MgSO_4$, filtered, and the solvent was evaporated *in vacuo*. The 1-chlorovinyl sulfoxides **1a-t** were isolated in an analytically pure state by column chromatography [diethyl ether/petroleum ether (40/60)].

(*Z*)-1-[2-Chloro-2-(methylsulfinyl)ethenyl]benzene (1a). ^{1}H-NMR: δ 2.81 (s, 3H, S(O)CH_3); 7.32-7.52 (m, 4H, $H_{arom.}$, CH=); 7.64-7.84 (m, 2H). ^{13}C-NMR: δ 39.48 (S(O)CH_3); 128.51, 128.63, 129.47, 129.65 (CH, CH=); 131.78 (q-C); 134.50 (=C).

(*Z*)-1-[2-Chloro-2-(methylsulfinyl)ethenyl]-4-chlorobenzene (1b). ^{1}H-NMR: δ 2.81 (s, 3H, S(O)CH_3); 7.40 (d, J=8.7, 2H); 7.40 (s, 1H, CH=); 7.70 (d, J=8.7, 2H). ^{13}C-NMR: δ 39.54 (S(O)CH_3); 127.28, 128.83, 130.70 (CH, CH=); 130.29, 135.28, 135.52 (q-C, =C). Anal. cald. for $C_9H_8Cl_2OS$ (235.13): C 45.97 H 3.43; found: C 46.25 H 3.52. M.p. 40-3°C.

(*Z*)-1-[2-Chloro-2-(methylsulfinyl)ethenyl]-4-methoxybenzene (1c). ^{1}H-NMR: δ 2.79 (s, 3H, S(O)CH_3); 3.85 (s, 3H, OCH_3); 6.94 (d, J=9.2, 2H); 7.35 (s, 1H, CH=); 7.75 (d, J=8.8, 2H). ^{13}C-NMR: δ 39.28 (S(O)CH_3); 55.01 (OCH_3); 113.82, 128.51 (CH); 124.30 (q-C); 131.20 (CH=); 131.60 (=C); 160.45 (C-O). Anal. cald. for $C_{10}H_{11}ClO_2S$ (230.71): C 52.06 H 4.81; found: C 51.90 H 4.73. M.p. 70-2°C.

(*Z*)-2-[2-Chloro-2-(methylsulfinyl)ethenyl]thiophene (1d). ^{1}H-NMR: δ 2.80 (s, 3H, S(O)CH_3); 7.12 (dd, J=3.8, J=5.2, 1H); 7.43 (d, J=3.8, 1H); 7.52 (d, J=5.2, 1H); 7.66 (s, 1H, CH=). ^{13}C-NMR: δ 39.77 (S(O)CH_3); 123.46, 127.08, 129.65, 132.22 (CH, CH=); 131.60, 134.96 (q-C, =C). Anal. cald. for $C_7H_7ClOS_2$ (206.70): C 40.67 H 3.41; found: C 40.57 H 3.39. M.p. 93-4°C.

1-Chloro-1-(methylsulfinyl)-1(*Z*),3(*E*)-hexadiene (1e). ^{1}H-NMR: δ 1.07 (t, J=7.2, 3H, CH_3); 2.12-2.32 (m, 2H, CH_2); 2.73 (s, 3H, S(O)CH_3); 6.08-6.48 (m, 2H, CH=CH); 7.02 (d, J=9.8, 1H, CH=). ^{13}C-NMR: δ 12.44 (CH_3); 24.84 (CH_2); 38.95 (S(O)CH_3); 121.65, 130.70, 145.91 (CH=); 132.48 (=C). Anal. cald. for $C_7H_{11}ClOS$ (178.68): C 47.06 H 6.21; found: C 46.77 H 6.38.

1-Chloro-1-(methylsulfinyl)-4-phenyl-1(*Z*),3(*E*)-butadiene (1e). ^{1}H-NMR: δ 2.78 (s, 3H, S(O)CH_3); 6.89-7.25 (m, 3H, diene); 7.34-7.53 (m, 5H, phenyl). ^{13}C-NMR: δ 39.2 (S(O)CH_3); 120.3; 127.0; 128.5; 129.0; 130.3 (CH=); 135.0; 135.5 (=C); 140.1 (=CH). M.p. 58-60°C.

(*Z*)-1-Chloro-1-(methylsulfinyl)-1-hexene [(*Z*)-**1g**]. ^{1}H-NMR: δ 0.92 (t, J=7.2, 3H, CH_3); 1.14-1.60 (m, 4H, $(CH_2)_2$); 2.37 (dt, J=7.7, J=7.2, 2H, CH_2); 2.71 (s, 3H, S(O)CH_3); 6.60 (t, J=7.2, 1H, CH=). ^{13}C-NMR: δ 13.35 (CH_3); 21.79, 27.56, 29.58 (CH_2); 38.92 (S(O)CH_3); 133.71 (CH=); 135.66 (=C).

(*E*)-1-Chloro-1-(methylsulfinyl)-1-hexene [(*E*)-**1g**]. ^{1}H-NMR: δ 0.92 (t, J=7.2, 3H, CH_3); 1.20-1.56 (m, 4H, $(CH_2)_2$); 2.24-2.60 (m, 2H, CH_2); 2.68 (s, 3H, S(O)CH_3); 6.30 (t, J=8.2, 1H, CH=). ^{13}C-NMR: δ 13.49 (CH_3); 21.87, 28.67, 30.87 (CH_2); 37.93 (S(O)CH_3); 136.48 (=C); 139.72 (CH=).

(*Z*)-1-[2-Chloro-2-(methylsulfinyl)ethenyl]cyclohexane [(*Z*)-**1h**]. ^{1}H-NMR: δ 1.04-1.40 (m, 5H, CH_2); 1.40-1.92 (m, 5H, CH_2); 2.60-2.84 (m, 1H, CH); 6.15 (d, J=10.3, 1H, CH=). ^{13}C-NMR: δ 24.76, 24.94, 25.05, 32.24, 32.56, 38.22, 38.28 ($(CH_2)_5$, CH, S(O)CH_3); 135.08 (=C); 144.63 (CH=). Anal. cald. for $C_9H_{15}ClOS$ (206.73): C 52.29 H 7.31; found: C 50.99 H 7.34.

(*E*)-1-[2-Chloro-2-(methylsulfinyl)ethenyl]cyclohexane [(*E*)-**1h**]. ^{1}H-NMR: δ 1.00-1.40 (m, 5H, CH_2); 1.40-1.94 (m, 5H, CH_2); 2.52-2.70 (m, 1H, CH); 2.71 (s, 3H, S(O)CH_3); 6.45 (d, J=8.2, 1H, CH=). ^{13}C-NMR: δ 24.99, 25.14, 25.29, 25.46, 31.13, 37.49, 39.10 ($(CH_2)_5$, CH, S(O)CH_3); 134.09 (=C); 138.11 (CH=).

(*Z*)-1-Chloro-1-(cyclohexylsulfinyl)-1-hexene [(*Z*)-**1i**]. ^{1}H-NMR: δ 0.92 (t, J=6.7, 3H, CH_3); 1.04-1.76, 1.76-2.00 (2xm, 14H, CH_2); 2.38 (dt, J=7.2, J=7.1, 2H, CH_2); 2.76-2.92 (m, 1H, S-CH); 6.50 (t, J=7.2, CH=). ^{13}C-NMR: δ 13.55 (CH_3); 22.08, 22.83, 25.02, 25.46, 26.54, 27.91, 29.92 (CH_2); 56.85 (S-CH); 132.33 (=C); 136.16 (CH=). Anal. cald. for $C_{12}H_{21}ClOS$ (248.10): C 57.93 H 8.51; found: C 58.29 H 8.84.

(*E*)-1-Chloro-1-(cyclohexylsulfinyl)-1-hexene [(*E*)-**1i**]. ^{1}H-NMR: δ 0.92 (t, J=7.2, 3H, CH_3); 1.20-1.40, 1.40-1.64, 1.64-2.04 (3xm, 12H, CH_2); 2.20-2.60 (m, 4H, CH_2); 2.92-3.08 (m, 1H, S-CH); 6.43 (dd, J=8.8, J=7.7, 1H, CH=). ^{13}C-NMR: δ 13.61 (CH_3); 21.99, 24.79, 25.35, 25.99, 29.03, 30.92 (CH_2); 58.31 (S-CH); 133.94 (=C); 142.29 (CH=).

[(1-Chloroethenyl)sulfinyl]benzene (1j). ^{1}H-NMR: δ 5.97 (d, J=3.1, (*Z*)-HC=); 6.46 (d, J=3.1, (*E*)-HC=); 7.44-7.64 (m, 3H); 7.74-7.80 (m, 2H). ^{13}C-NMR: δ 117.35 (H_2C=); 125.74, 129.06, 131.93 (CH); 141.01, 144.69 (q-C, =C). Anal. cald. for C_8H_7ClOS (186.66): C 51.48 H 3.78; found: C 51.32 H 3.81.

[(1-Chloro-1(*Z*),3(*E*)-pentadienyl)sulfinyl]benzene (1k). ^{1}H-NMR: δ 1.90 (d, J=5.6, 3H, CH_3); 6.12-6.48 (m, 2H, CH=CH); 7.22 (d, J=9.2, 1H, CH=); 7.48-7.60 (m, 3H); 7.64-7.76 (m, 2H). ^{13}C-NMR: δ 18.84 (CH_3); 124.60, 125.36, 129.06, 131.58, 140.07 (CH, CH=); 133.44, 141.74 (q-C, =C).

(*Z*)-[(1-Chloro-1-propenyl)sulfinyl]benzene (1l). ^{1}H-NMR: δ 1.95 (d, J=7.2, 3H, CH_3); 6.86 (q, J=6.6, 1H, CH=); 7.44-7.60 (m, 3H); 7.60-7.72 (m, 2H). ^{13}C-NMR: δ 13.90 (CH_3); 125.06, 128.89, 130.17, 131.40 (CH, CH=); 137.82, 141.33 (q-C, =C).

(*Z*)-[(1-Chloro-1-pentenyl)sulfinyl]benzene (1m). ^{1}H-NMR: δ 0.96 (t, J=7.2, 3H, CH_3); 1.40-1.64 (m, 2H, CH_2); 2.33 (dt, J=7.2, J=7.2, 2H, CH_2); 6.80 (t, J=7.2, 1H, CH=); 7.44-7.60 (m, 3H); 7.52-7.80 (m, 2H). ^{13}C-NMR: δ 13.46 (CH_3); 21.11, 30.14 (CH_2); 125.15, 128.89, 131.43, 134.67 (CH, CH=); 136.95, 141.47 (q-C, =C). Anal. cald. for $C_{11}H_{13}ClOS$ (228.74): C 57.76 H 5.73; found: C 57.48 H 5.73.

(*Z*)-[(1-Chloro-1-hexenyl)sulfinyl]benzene (1n). ^{1}H-NMR: δ 0.92 (t, J=7.7, 3H, CH_3); 1.20-1.40 (m, 4H, CH_2); 2.35 (dt, J=7.2, J=7.7, 2H, CH_2); 6.80 (t, J=7.2, 1H, CH=); 7.44-7.60 (m, 3H); 7.60-7.72 (m, 2H). ^{13}C-NMR: δ 13.64 (CH_3); 22.11, 28.03, 29.87 (CH_2); 125.27, 128.98, 131.52, 135.02 (CH, CH=); 136.77, 141.56 (q-C, =C).

1-[(1-Chloroethenyl)sulfinyl]-4-methylbenzene (1o). ^{1}H-NMR: δ 2.42 (s, 3H, CH_3); 5.96 (d, J=2.6, 1H, (*Z*)-HC=); 6.44 (d, J=3.1, 1H, (*E*)-HC=); 7.32 (d, J=8.2, 2H); 7.60 (d, J=8.2, 2H). ^{13}C-NMR: δ 21.44 (CH_3); 117.06 (H_2C=); 125.73, 129.85 (CH); 142.76, 144.86 (q-C, =C). One q-C not resolved.

(*Z*)-1-[(1-Chloro-2(*E*)-phenylethenyl)sulfinyl]-4-methylbenzene (1p). ^{1}H-NMR: δ 2.41 (s, 3H, CH_3); 7.31 (d, J=7.7, 2H); 7.32-7.48 (m, 3H), 7.62 (s, 1H, CH=); 7.64 (d, J=7.2, 2H); 7.72-7.84 (m, 2H); ^{13}C-NMR: δ 21.23 (CH_3), 125.53, 128.36, 128.57, 129.50, 129.56, 129.68 (CH, CH=); 131.84, 135.25, 138.41, 142.32 (q-C, =C). Anal cald. for $C_{15}H_{13}ClOS$ (276.79): C 65.09 H 4.73; found: C 65.11 H 4.75. M.p. 69-72°C.

(*Z*)-1-[2-Chloro-2-(*p*-tolylsulfinyl)ethenyl]-4-methoxybenzene (1q). ^{1}H-NMR: δ 2.41 (s, 3H, CH_3); 3.83 (s, 3H, OCH_3); 6.93 (d, J=7.2, 2H); 7.31 (d, J=8.2, 2H); 7.55 (s, 1H, CH=); 7.62 (d, J=8.2, 2H); 7.74 (d, J=7.2, 2H). ^{13}C-NMR: δ 21.32 (CH_3); 55.16 (OCH_3); 113.91, 125.53, 128.98, 129.74, 131.46 (CH, CH=); 124.63, 132.60, 138.67, 142.23, (q-C, =C); 160.66 (O-C). Anal. cald. for $C_{16}H_{15}ClO_2S$ (306.81): C 62.64 H 4.93; found: C 62.51 H 4.91. M.p. 80-2°C.

(*Z*)-1-[2-Chloro-2-(*p*-tolylsulfinyl)ethenyl]-4-(methylthio)benzene (1r). ^{1}H-NMR: δ 2.41 (s, 3H, CH_3); 2.49 (s, 3H, SCH_3); 7.23 (d, J=8.7, 2H); 7.31 (d, J=8.2, 2H); 7.62 (d, J=8.7, 2H); 7.56 (s, 1H, CH=); 7.69 (d, J=8.2, 2H). ^{13}C-NMR: δ 14.49 (SCH_3); 21.03 (CH_3); 125.09, 125.24, 128.16, 129.47, 129.65 (CH, CH=); 134.09, 138.26, 141.27. 142.00, 142.09 (q-C, =C). Anal. cald. for $C_{16}H_{15}ClOS_2$ (322.87): C 59.92 H 4.68; found: C 59.80 H 4.64. M.p. 105-6°C.

1-[(1-Chloro-1(*Z*),3(*E*)-pentadienyl)sulfinyl]-4-methylbenzene (1s). ^{1}H-NMR: δ 1.89 (d, J=5.1, 3H, CH_3); 2.41 (s, 3H, CH_3); 6.12-6.48 (m, 2H, CH=CH); 7.18 (d, J=9.8, 1H, CH=); 7.31 (d, J=8.2, 2H); 7.56 (d, J=8.2, 2H). ^{13}C-NMR: δ 18.78 (CH_3); 21.35 ($CH_{3,p\text{-tolyl}}$); 124.57, 125.38, 129.74, 131.08, 139.72 (CH, CH=); 133.47, 138.47, 142.17 (q-C, =C). Anal. cald. for $C_{12}H_{13}ClOS$ (240.75): C 59.87 H 5.44; found: C 60.01 H 5.43.

(*Z*)-1-[(1-Chloro-1-hexenyl)sulfinyl]-4-methylbenzene (1t). ^{1}H-NMR: δ 0.91 (t, J=7.2, 3H, CH_3); 1.20-1.64 (m, 4H, $(CH_2)_2$); 2.34 (dt, J=7.6, J=7.2, 2H, CH_2); 2.41 (s, 3H, CH_3); 6.78 (t, J=7.2, 1H, CH=); 7.30 (d, J=8.7, 2H); 7.55 (d, J=8.2, 2H). ^{13}C-NMR: δ 13.64 (CH_3); 21.35, 22.11, 27.97, 29.90 (CH_2, $CH_{3,p\text{-tolyl}}$); 125.36, 129.71, 134.44 (CH, CH=); 136.83, 138.38, 142.15 (q-C, =C).

(*Z*/*E*)-1-[((1-Chloro-2-cyclohexyl)ethenyl)sulfinyl]-4-methylbenzene (*Z*- and *E*-**1u**). ^{1}H-NMR: δ 1.04-1.48 (m, CH_2), 2.41 (s, CH_3); 2.40-2.64 (m, CH); 2.92-3.04 (m, CH); 6.15 (d, J=10.8, (*E*)-CH=); 6.63 (d, J=9.2, (*Z*)-CH=); 7.20-7.36 (m); 7.40-7.56 (m). ^{13}C-NMR: δ 21.35 (CH_3); 25.20, 31.19, 37.67 ((*Z*)-CH_2); 25.55, 32.56, 32.65, 38.66 ((*E*)-CH_2); 124.51, 125.38, 129.71 (CH); 138.91 ((*Z*)-CH=); 135.14, 136.39, 137.82, 138.44, 141.54, 142.12, 145.39 (q-C, =C, (*E*)-CH=). Anal. cald. for $C_{15}H_{19}ClOS$ (282.83): C 63.70 H 6.77; found: C 63.87 H 6.96.

1-[(1-Chloroethenyl)sulfinyl]-4-(trifluoromethyl)benzene (1v). ^{1}H-NMR: δ 6.01 (d, J=3.1, 1H, (*Z*)-HC=); 6.48 (d, J=3.1, 1H, (*E*)-HC=); 7.78-7.90 (m, 4H). ^{13}C-NMR: δ 118.3 (H_2C=); 123.1 (q, J_{CF}=256, CF_3); 125.8, 126.1 (CH); 133.8 (q, J_{CF}=34, C-CF_3); 144.3, 145.5 (=C, q-C).

(*Z*)-1-[(1-Chloro-1-pentenyl)sulfinyl]-4-(trifluoromethyl)benzene (1w). ^{1}H-NMR: δ 0.96 (t, J_{HH}=7.2, 3H, CH_3); 1.48 (m, 2H, CH_2); 2.34 (dt, J_{HH}=7.2, 2H, CH_2); 6.84 (t, J_{HH}=7.2, 1H, CH); 7.79 (s, 4H, arom.). ^{13}C-NMR: δ 13.4 (CH_3); 21.0 (CH_2); 30.2 (CH_2); 125.5 (CH, arom., *o*-C); 125.6 (CH) 125.9 (q, J_{CF}=0.1, CH, arom., *m*-CH); 133.2 (q-C, q, J_{CH}=0.6, arom., *p*-C); 136.2 (CH, alkene, C-2); 141.4 (q-C, arom., *i*-C); 145.9 (q-C, =C, C-1).

(*E*/*Z*)-[(1-Chloro-1-pentenyl)thio]benzene ((*Z*)- and (*E*)-**10**). Compound **10** was prepared according to the Horner-Wittig procedure described above from phosphine oxide **7c** and *n*-butyric aldehyde. ^{1}H-NMR: δ 0.95 (t, J=7.2, CH_3); 0.97 (t, J=7.2, CH_3); 1.36-1.60 (m, CH_2); 2.16-2.40 (m, CH_2); 6.30 (t, J=7.2, CH=); 7.12-7.44 (m, $H_{arom.}$, CH=). ^{13}C-NMR: δ 13.73 (CH_3); 21.49, 22.22, 32.30, 32.97 (CH_2); 127.05, 127.20, 129.10, 129.50, 129.59 (CH); 139.75, 141.09 (S-C). =C not detected.

(*Z*)-[(1-Chloro-1-pentenyl)sulfonyl]benzene (**11**). Compound **11** was prepared according to the Horner-Wittig procedure described above from phosphine oxide **8a** and *n*-butyric aldehyde. ^{1}H-NMR: 0.96 (t, J=7.7, 3H, CH_3); 1.44-1.64 (m, 2H, CH_2); 2.31 (dt, J=7.7, J=7.2, 2H, CH_2); 7.23 (t, J=7.2, 1H, CH=); 7.48-7.72 (m, 3H); 7.94 (dd, J=1.6, J=8.0, 2H). ^{13}C-NMR: δ 13.52 (CH_3); 20.79, 30.63 ($(CH_2)_2$); 128.63, 129.01, 133.88 (CH); 132.51, 137.27 (q-C, =C); 140.36 (CH=).

[(1-Chloroethenyl)sulfonyl]benzene (**12**). Compound **12** was prepared according to the Horner-Wittig procedure described above from phosphine oxide **8a** and carefully dried paraformaldehyde. ^{1}H-NMR: δ 6.07 (d, J=3.1, (*Z*)-CH=); 6.72 (d, J=2.6, 1H, (*E*)-CH=); 7.48-7.76 (m, 3H); 7.84-8.00 (m, 2H). ^{13}C-NMR: δ 123.98, 128.80, 129.12, 134.29 (CH, CH_2=); 136.19, 139.98 (q-C, =C).

Table 5. Selected Geometric Data of **1c**. E.s.d's are given in parentheses.

Bond lengths (Å)			
C(11)-C(21)	1.314(5)	C(12)-C(22)	1.314(7)
C(11)-S(1)	1.794(5)	C(12)-S(2)	1.790(5)
C(11)-Cl(1)	1.716(5)	C(12)-Cl(2)	1.734(7)
S(1)-C(91)	1.771(8)	S(2)-C(92)	1.786(6)
S(1)-O(11)	1.474(5)	S(2)-O(12)	1.487(3)
C(21)-C(31)	1.458(6)	C(22)-C(32)	1.468(6)
C(61)-O(21)	1.359(5)	C(62)-O(22)	1.354(5)
O(21)-C(101)	1.423(7)	O(22)-C(102)	1.43(1)
Bond angles (°)			
C(11)-C(21)-C(31)	133.1(4)	C(22)-C(12)-C(32)	143.2(6)
C(21)-C(11)-Cl(1)	126.7(4)	C(22)-C(12)-Cl(2)	126.0(4)
C(21)-C(11)-S(1)	118.7(4)	C(22)-C(12)-S(2)	118.5(5)
C(11)-S(1)-O(11)	109.2(3)	C(12)-S(2)-O(12)	107.5(2)
C(11)-S(1)-C(91)	98.2(3)	C(12)-S(2)-C(92)	99.8(3)
C(91)-S(1)-O(11)	106.3(3)	C(92)-S(2)-O(12)	105.7(2)
Dihedral angles (°)			
C(11)-C(21)-C(31)-C(41)	5(1)	C(12)-C(22)-C(32)-C(42)	177.9(4)
Cl(1)-C(11)-C(21)-C(31)	4(1)	Cl(2)-C(12)-C(22)-C(32)	3.0(6)

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(*Received in UK* 15 *April* 1997; *revised* 2 *June* 1997; *accepted* 5 *June* 1997)