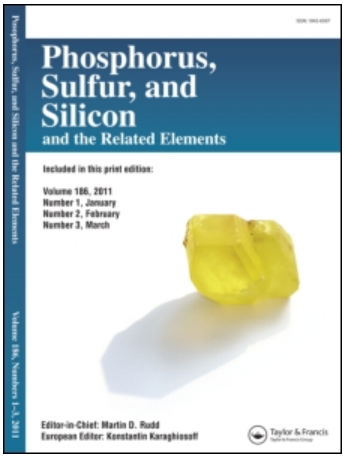

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SYNTHESIS AND THERMOLYSIS OF *meso*- AND *dl*-1,2-DIPHENYL-1,2-DIVINYLDIPHOSPHANE DISULFIDES

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SYNTHESIS AND THERMOLYSIS OF *meso*- AND *dl*-1,2-DIPHENYL-1,2-DIVINYLDIPHOSPHANE DISULFIDES

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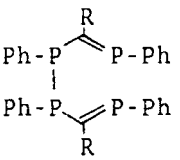
meso- and *dl*-1,2-Diphenyl-1,2-divinyldiphosphane disulfides **2a** were synthesized independently from the corresponding 1,2-bis-(2-hydroxyethyl)-1,2-diphenyldiphosphane disulfides via the ditosylate in 78 and 80% yields, respectively. ^{1}H-NMR spectra of *meso*- and *dl*-**2a** show that the rotamer with *trans* relationship of P=S groups is preferred in solution. Thermolyses were carried out in 1-hexanol to give *O*-hexyl 2-(phenylvinylphosphinothioyl)ethylphenylphosphinothioate and *O*-hexyl phenylvinylphosphinothioate in 33 and 12% yields, respectively. The possible mechanisms are discussed.

INTRODUCTION

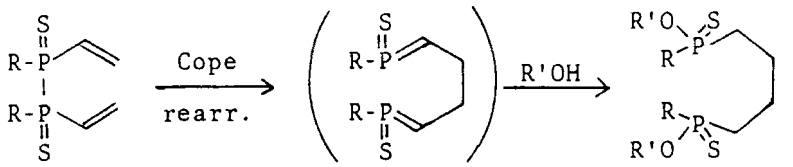
The Cope rearrangement involving a hetero atom has been an excellent method for the stereoselective synthesis of organic compounds. In particular, the Claisen rearrangement of allyl vinyl ether groups is an important step in the synthesis of a number of natural products.[1]



1 : R= NPhSiMe$_3$

FIGURE 1 *dl*-Diphosphane **1**.

Appel *et al.*[2] have observed, by use of ^{31}P-NMR spectroscopic, such a hetero-Cope rearrangement in *dl*-diphosphane **1**. Recently, Loewus found that sodium allylvinylphosphinate can rearrange to a reactive intermediate, sodium pent-4-enemetaphosphinate, which can be trapped with water to give sodium pent-4-enephosphonate.[3]



(1)

2a: R=Ph **3** **4**

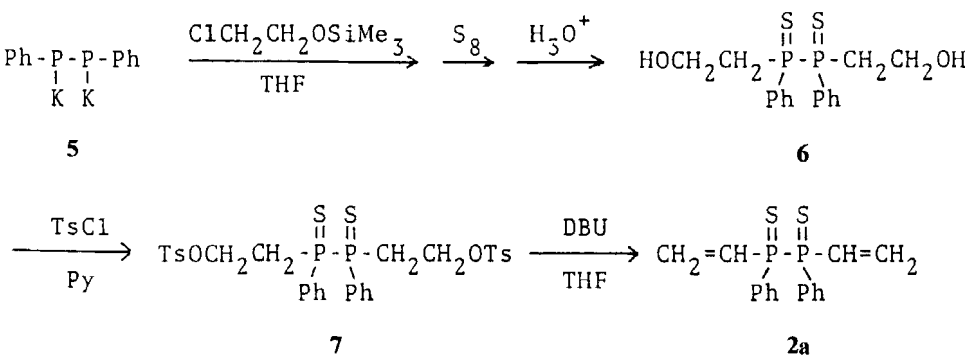
1,2-Disubstituted 1,2-divinyldiphosphane disulfide **2** would be expected to undergo such a type of Cope rearrangement as shown in Eq. (1) to generate an analogous reactive species **3** containing the monomeric metathiophosphinate moiety ($R—P(S) = CR'_2$) which has been investigated in our laboratory.[4]

We wish to report the synthesis of *meso*- and *dl*-1,2-diphenyl-1,2-divinyldiphosphane disulfides **2a** and their thermolysis in alcohol.

RESULTS AND DISCUSSIONS

Synthesis of **2a**

Direct preparation of **2a** by the anomalous Grignard reaction[5] using phenylphosphonothioyl dihalide and vinylmagnesium bromide resulted in quite poor yield of **2a**. Separation of the diastereomers was difficult; therefore, a novel synthetic route for **2a** has been developed as shown in the following scheme.



5 **6** **7** **2a**

SCHEME 1 Synthetic route of **2a**.

Reaction of 1,2-diphenyl-1,2-dipotassiodiphosphane **5** with 2 equivalents of 2-chloroethoxytrimethylsilane, followed by sulfurization and acid desilylation gave a mixture of *meso*- and *dl*-1,2-bis(2-hydroxyethyl)-1,2-diphenyldiphosphane disulfides **6** which could be separated and purified by column chromatography on SiO_2. Yields of *meso*- and *dl*-**6** were 28 and 28%, respectively. The usual tosylation of each diol (*meso*- or *dl*-**6**) afforded almost quantitatively the corresponding ditosylate (*meso*- or *dl*-**7**) which was converted to the divinyl derivative (*meso*- or *dl*-**2a**) in very good yield by treatment with 2 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The yields, melting points, and ^{31}P-NMR data are shown in Table I. The present method has some merits, that is, easier separation of diastereomers in **6** and fairly good yields of all steps.

TABLE I

Melting points, yields, and ^{31}P-NMR spectral data for diphosphane disulfides

Compound	Mp (°C)	Yield (%)	δ_p[a]
meso-**6**	134–136	28	38.6
dl-**6**	102–104	28	41.1
meso-**7**	140–141	87	36.1
dl-**7**	–[b]	89	38.4
meso-**2a**	184–186	90	34.8
dl-**2a**	135–137	90	34.3

[a] ppm from 85% H_3PO_4.
[b] Not crystallized.

Structure and Conformation of **2a**

It has been confirmed that diphosphanes (RR'P—PRR') exist as a diastereomeric mixture, e.g., meso and dl forms,[6] that the internal rotation about the P—P bond is very rapid on the NMR time scale,[7] and that the gauche relationship of the lone pairs on phosphorus atoms is the predominant factor among those considered to stabilize the rotamer.[8] Also, it has been reported that diphosphanes have a lower barrier of inversion at the phosphorus atom than monophosphanes, which can be explained reasonably by the contribution of p_π-d_π hybridization to the P—P bond.[9]

However, in diphosphane disulfides without lone pairs on phosphorus atom, dipole–dipole repulsion must play an important role in stabilization of conformers, so that the conformer with a trans relationship of two P=S groups seems to be favored in solution. It has been deduced from X-ray analysis that the higher melting diastereomer is the meso form and exists as a conformer with centrosymmetry in the solid state.[10] Detailed investigation of ^{1}H-NMR spectra of both diastereomers,

TABLE II

^{1}H-NMR spectral data of diphosphane disulfides

Compound	R Groups α-protons	R Groups β-protons	Ph Groups *meta* and *para* protons	Ph Groups *ortho* protons	Others
meso-**6**	2.36–2.83	3.38–3.88	7.41–7.75	8.00–8.31	2.05[a]
dl-**6**	2.46–3.63	3.86–4.33	7.02–7.40	7.40–7.75	3.03[a]
meso-**7**	2.06–2.63 2.63–3.13	3.66–4.16	7.33–7.73[b]	7.86–8.20	2.43,[c] 7.06–7.33[d]
dl-**7**	2.82–3.18	4.08–4.63	7.00–7.38[e]	7.38–7.78	2.42,[c] 7.60–7.78[f]
meso-**2a**	5.90–7.33[g]		7.33–7.70	7.86–8.20	
dl-**2a**	6.08–7.23[g]		7.23–7.53	7.53–7.90	

[a] Broad singlet due to OH.
[b] Signals due to *ortho* protons of Ts groups superimposed here.
[c] Singlet due to methyl protons of Ts groups.
[d] Signals due to *meta* protons of Ts groups.
[e] Signals due to *meta* protons of Ts groups superimposed here.
[f] Signals due to *ortho* protons of Ts groups.
[g] Multiplet due to vinyl groups cannot be resolved.

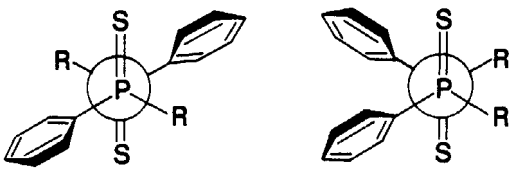


FIGURE 2 The most predominant rotamer.

which were prepared in the present work, showed the following characteristic trend (Table II): In general, the signal due to the ortho protons of a phenyl group attached to a P=S group should be observed at lower field than those due to meta and para protons because of the strong magnetic anisotropy of the P=S group.

However, ^{1}H-NMR spectra of the lower melting diastereomers, that is, dl forms, showed a reduced deshielding effect and a higher chemical shift; whereas signals due to R groups of the higher melting meso forms were observed at higher field than those of the dl forms. These phenomena can be interpreted as follows.

Since I (*meso*) and II (*dl*) seem to be the predominant rotamers in the meso and dl forms, respectively, the phenyl and R groups in the former and the phenyl groups in the latter become gauche to each other. Therefore, the probability that the protons of the phenyl group, especially ortho protons, overlap the plane of the adjacent phenyl group may be larger in the dl than in the meso form, so that signals due to the ortho protons of the phenyl group shift to high field in the dl form by an anisotropic shielding effect of the diamagnetic ring current. The shift of signals due to the R groups of the meso form can be explained similarly. It is interesting to point out that a conformer with P=S groups trans is prefers to others in both diastereomers, not only in the solid state but also in solution.

As reported previously,[11] meso and dl diastereomers had distinct chemical shifts in their ^{31}P-NMR spectra. The meso-form signal appears at higher field than the dl signal in **6** and **7**, but not in **2a**. Therefore, ^{31}P-NMR spectroscopy seems not to be a useful method to determine the stereochemistry of diastereomers. Table III shows ^{1}H noise-decoupled ^{13}C-NMR spectral data of *meso*- and *dl*-**2a**. It is interesting to note

TABLE III

^{1}H-Noise decoupled ^{13}C-NMR spectral data of *meso*- and *dl*-**2a**

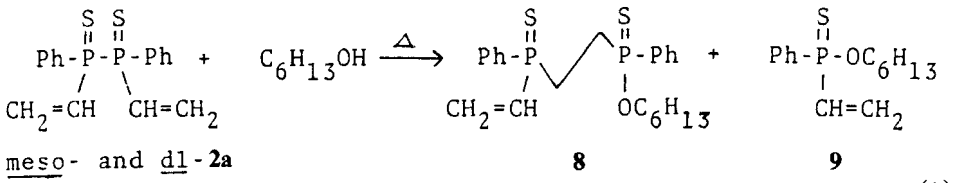
Carbon	*meso*-**2a**	*dl*-**2a**
α-C	125.18[a](70.2, 14.0)[b]	125.18 (70.8, 14.7)
β-C	138.43 (1.7, 1.7)	138.21 (3.7, 3.7)
ipso-C	127.21 (74.0, 11.5)	126.90 (72.6, 11.0)
ortho-C	132.93 (9.4, 1.2)	132.13 (9.2, 1.2)
meta-C	128.08 (12.7, 1.2)	127.87 (12.1, 1.2)
para-C	132.49 (3.8, 2.1)	132.21 (3.1, 1.2)

[a]δ ppm from tetramethylsilane as internal standard.
[b]$J_{CP}\alpha$ and $J_{CP}\beta$ are shown in parentheses in Hz.

that the signals due to the carbons of *meso*-**2a** are observed at lower field than those of *dl*-**2a** and that the coupling constants between carbons of the phenyl groups and phosphorus nuclei are larger in *meso*-**2a** than in *dl*-**2a**, whereas those between the carbons of vinyl groups and phosphorus nuclei are smaller in *meso*-**2a** than in *dl*-**2a**.

Thermolysis of **2a** *in 1-hexanol*

A solution of *meso*-**2a** in 1-hexanol was refluxed for 3–4 h to give *O*-hexyl 2-(phenylvinylphosphinothioyl)ethylphenylphosphinothioate **8** and *O*-hexyl phenylvinylphosphinothioate **9** as identified products in 25 and 12% yields, respectively. When *dl*-**2a** was heated, a quite similar result was obtained. The reaction proceeded even at 120°C, but it took 2–3 days and yields of **8** and **9** were 33 and 12%, respectively.



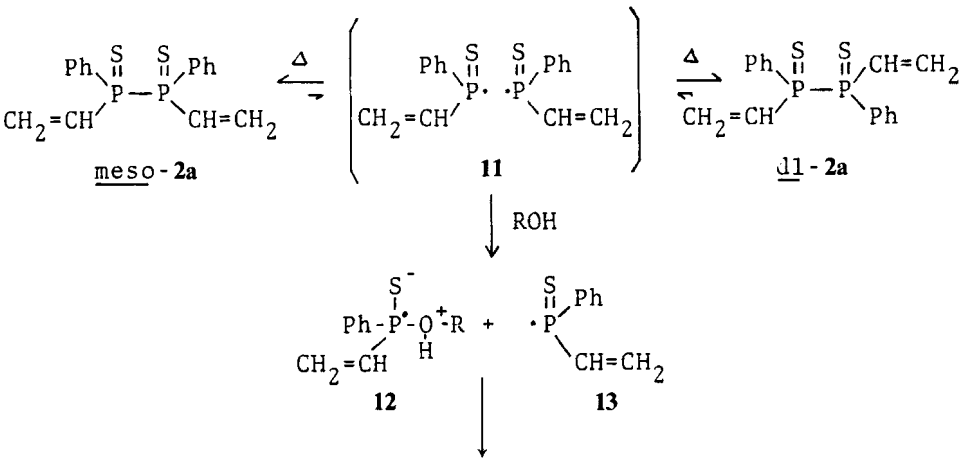
meso- and dl-**2a** **8** **9**

(2)

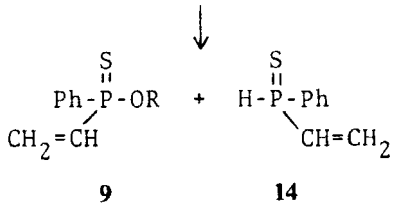
There was no evidence for formation of **4a** (R = Ph, R′ = C_6H_{13}), as expected from the Cope rearrangement as shown in Eq. (1). When the reaction was monitored by ^{31}P-NMR spectroscopy, isomerization between *meso*- and *dl*-**2a** was first observed, then peaks of the products gradually appeared, with disappearance of the starting material, which maintained the equilibrium ratio of both isomers.

Addition of anhydrous zinc bromide accelerated not only the isomerization, but also the formation of **8** and **9** in the presence of alcohol. Possible mechanisms of this reaction are shown in the following scheme.

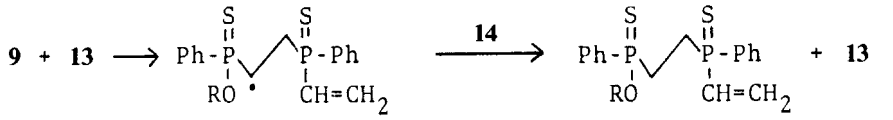
Path (a): Radical process



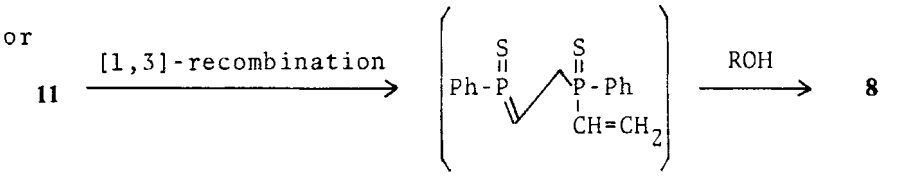
SCHEME 2 Possible mechanisms.



9 **14**

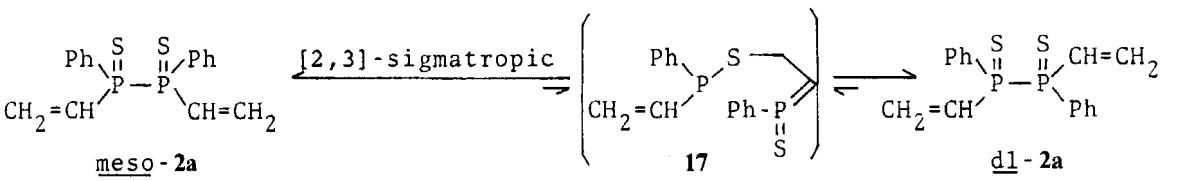


15 **8**

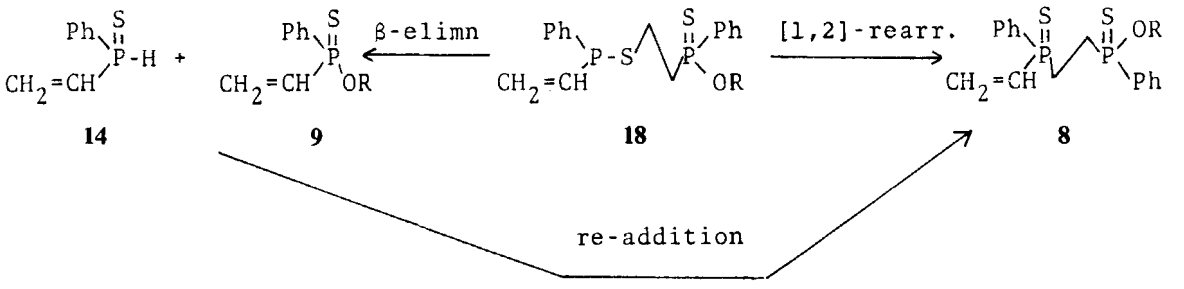


16

Path (b): Concerted process



meso-**2a** **17** dl-**2a**



14 **9** **18** **8**

Path (a) includes the formation of caged radical pair **11** by homolysis of the P—P bond, formation of **9** and **14** via intermediate **12** formed by electrophilic attack of free phosphinothioyl radical **13** on the lone pair of the alcohol oxygen atom and formation of **8** by radical-chain reaction where **13** acts as chain carrier. The formation of **8** may proceed via **16** formed by [1,3]-recombination of **11**.

On the other hand, path (b) includes formation of **17** by [2,3]-sigmatropic rearrangement, well known in allyl sulfoxides,[12] nucleophilic addition of alcohol to the C=P bond of **17** to afford **18**, which gives **9** by β-elimination of **14** and **8** by [1,2]-rearrangement, or re-addition of **14** to **9**. Intermediate **12** in path (a) has been postulated in methanolic photolyses of tetraphenyldiphosphane disulfide[13] and the insertion product of phenylphosphinothioylidene (Ph—P=S) to the OH bond of methanol, *O*-methyl phenylphosphinothioate.[14] Also, [2,3]-sigmatropic rearrangement in path (b) has been proposed in the racemization of optically active allylmethylphenylphosphane sulfide.[15]

Effects of zinc bromide can be explained in both mechanisms, that is, in path (a) chelation of S atoms makes the ground state unstable and results in accelerating isomerization and coordination of the P=S bond of **13** to $ZnBr_2$ which increases the electrophilicity of **13** toward alcohol, whereas in path (b) coordination of P=S to $ZnBr_2$ lowers the energy of the LUMO of the acceptor to accelerate the [2,3]-sigmatropic rearrangement[16] and also activates the C=P bond of **17**. From the analogy with photolysis of tetraphenyldiphosphane disulfide in methanol, and the necessity of more drastic conditions for the [2,3]-sigmatropic rearrangement, path (a) is preferred to path (b); however, path (b) can not be ruled out completely. Further investigations are in progress into the reason the [3,3]-sigmatropic rearrangement, Cope rearrangement, does not occur in the present system.

EXPERIMENTAL

All melting points are uncorrected. ^{1}H-NMR spectra were measured with a Varian EM-390 spectrometer using tetramethylsilane (TMS) as internal standard. ^{1}H-Noise decoupled ^{13}C- and ^{31}P-NMR spectra were measured with a JEOL FX-90Q spectrometer using TMS as internal standard and 85% H_3PO_4 as external standard, respectively. Low and high resolution mass spectra were measured with Hitachi RMU-6L and JEOL D-300 mass spectrometers, respectively. IR spectra were recorded with a Hitachi 260-30 spectrometer.

Preparation of 1,2-bis(2-hydroxyethyl)-1,2-diphenyldiphosphane disulfide **6**. Into a suspension of 1,2-diphenyl-1,2-dipotassiodiphosphane **5** prepared from tetraphenylcyclotetraphosphane[17] (4.65 g, 10.18 mmol) and potassium metal (1.68 g, 43.1 mmol) in freshly distilled THF (50 ml) was added a solution of 2-chloroethoxytrimethylsilane[18] (6.60 g, 43.0 mmol) in THF (20 ml) drop by drop at room temperature for 1 h under argon atmosphere. The reaction mixture was stirred overnight, then sulfur (1.40 g, 43.2 mmol) was added into the reaction mixture and the mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure, the residue was dissolved in CH_2Cl_2 again, and the CH_2Cl_2 solution was treated with dilute HCl in order to desilylate the corresponding silyl ether of **6**. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent column chromatography on (SiO_2, $CHCl_3$) gave *meso*- and *dl*-**6** in 28 and 28% yields, respectively.

meso-**6**: mp 134–136°C (CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): δ 2.05 (bs, 2 H, OH), 2.36–2.83 (m, 4 H, PCH_2CH_2O), 3.38–3.88 (m, 4 H, PCH_2CH_2O), 7.41–7.75 (m, 6 H, *meta* and *para* protons), and 8.00–8.31 (m, 4 H, *ortho* protons). ^{31}P-NMR ($CDCl_3$): δ_p 38.6 ppm. IR (KBr disc): ν_{OH} 3300 cm^{-1}. Mass spectrum (70 eV): m/e 370 (M^+, 1.4%) and 79 ($S{=}P^+{=}O$, 100%). High resolution mass spectrum: m/e Found: 370.0414. Calcd. for $C_{16}H_{20}O_2P_2S_2$: 370.0379. Elementary analysis: Found: C, 51.74; H, 5.64%. Calcd. for $C_{16}H_{20}O_2P_2S_2$: C, 51.88; H, 5.45%.

dl-**6**: mp 102–104°C (CH_2Cl_2 : EtOH = 1 : 1). ^{1}H-NMR ($CDCl_3$): δ 2.46–3.63 (m, 4 H, PCH_2CH_2O), 3.03 (bs, 2 H, OH), 3.86–4.33 (m, 4 H, PCH_2CH_2O), 7.02–7.40 (m, 6 H, *meta* and *para* protons), and 7.40–7.75 (m, 4 H, *ortho* protons). ^{31}P-NMR ($CDCl_3$): δ_p 41.1 ppm. IR (KBr disc): ν_{OH} 3250 cm^{-1}. Mass spectrum (70 eV): m/e 370 (M^+, 2.1%) and 79 ($S{=}P^+{=}O$, 100%). High resolution mass spectrum: m/e Found: 370.0342. Calcd. for $C_{16}H_{20}O_2P_2S_2$: 370.0379.

Preparation of 1,2-diphenyl-1,2-bis(2-tosyloxyethyl)diphosphane disulfide **7**. A mixture of *meso*-**6** (3.76 g, 10.2 mmol) and *p*-toluenesulfonyl chloride (5.7 g, 30.0 mmol) in pyridine (50 ml) was stirred at 0°C for 2 days. The reaction mixture was treated with dilute HCl in order to remove pyridine and the ditosylate was extracted with CH_2Cl_2. After removal of CH_2Cl_2, the residual solid was recrystallized from $CHCl_3$—EtOH (1 : 1) to give 5.92 g of *meso*-**7** in 87% yield.

meso-**7**: mp 140–141°C ($CHCl_3$: EtOH = 1 : 1). ^{1}H-NMR ($CDCl_3$): δ 2.43 (s, 6 H, $-CH_3$), 2.06–2.63 and 2.63–3.13 (m, 4 H, PCH_2CH_2O), 3.66–4.16 (m, 4 H, PCH_2CH_2O), 7.06–7.33 (m, 4 H, *meta* protons of Ts groups), 7.33–7.73 (m, 10 H, *meta* and *para* protons of Ph groups and *ortho* protons of Ts groups), and 7.86–8.20 (m, 4 H, *ortho* protons of Ph groups). ^{31}P-NMR ($CDCl_3$): δ_p 36.1 ppm. IR (KBr disc): ν_{SO_2} 1365 and 1180 cm^{-1}. Elementary analysis: Found: C, 52.79; H, 4.93%. Calcd. for $C_{30}H_{32}O_6P_2S_4$: C, 53.08; H, 4.76%.

dl-Ditosylate **7** was similarly obtained from *dl*-**6** in 89% yield as viscous oil. It was used for detosylation without further purification.

dl-**7**: ^{1}H-NMR ($CDCl_3$): δ 2.42 (s, 6 H, $-CH_3$), 2.82–3.18 (m, 4 H, PCH_2CH_2O), 4.08–4.63 (m, 4 H, PCH_2CH_2O), 7.00–7.38 (m, 10 H, *meta* and *para* protons of Ph groups and *meta* protons of Ts groups), 7.38–7.78 (m, 4 H, *ortho* protons of Ph groups), and 7.60–7.78 (m, 4 H, *ortho* protons of Ts groups). ^{31}P-NMR ($CDCl_3$): δ_p 38.4 ppm. IR (Neat): ν_{SO_2} 1365 and 1180 cm^{-1}. Mass spectra of *meso*- and *dl*-**7** gave no molecular ion peak.

Preparation of 1,2-diphenyl-1,2-divinyldiphosphane disulfide **2a**. Into a solution of *meso*-**7** (4.07 g, 6.00 mmol) in THF (100 ml) was added dropwise a solution of DBU (1.82 g, 12.0 mmol) in THF (20 ml) at room temperature for 1 h with stirring. After usual work-up, recrystallization from $CHCl_3$—EtOH (1 : 1) afforded *meso*-**2a** in 90% yield.

meso-**2a**: mp 184–186°C ($CHCl_3$: EtOH = 1 : 1). ^{1}H-NMR ($CDCl_3$): δ 5.90–7.33 (m, 6 H, vinyl protons), 7.33–7.70 (m, 6 H, *meta* and *para* protons), and 7.86–8.20 (m, 4 H, *ortho* protons). ^{31}P-NMR ($CDCl_3$): δ_p 34.8 ppm. Mass spectrum (70 eV): m/e 334 (M^+, 33%) and 162 ($PhP^+(CH{=}CH_2)_2$, 100%). High resolution mass spectrum: m/e Found: 334.0180. Calcd. for $C_{16}H_{16}P_2S_2$: 334.0169. Elementary analysis: Found: C, 57.23; H, 5.02%. Calcd. for $C_{16}H_{16}P_2S_2$: C, 57.47; H, 4.83%. IR (KBr disc): $\nu_{C=C}$ 1595 cm^{-1}.

dl-**2a** was obtained similarly from *dl*-**7** in 85% yield. *dl*-**2a**: mp 135–137°C ($CHCl_3$: EtOH = 1 : 3). ^{1}H-NMR ($CDCl_3$): δ 6.08–7.23 (m, 6 H, vinyl protons), 7.23–7.53 (m, 6 H, *meta* and *para* protons), and 7.53–7.90 (m, 4 H, *ortho* protons). ^{31}P-NMR ($CDCl_3$): δ_p 34.3 ppm. Mass spectrum (70 eV): m/e 334 (M^+, 31%) and 162 ($PhP^+(CH{=}CH_2)_2$, 100%). High resolution mass spectrum: m/e Found: 334.0178. Calcd. for $C_{16}H_{16}P_2S_2$: 334.0169. Elementary analysis: Found: C, 57.19; H, 4.97%. Calcd. for $C_{16}H_{16}P_2S_2$: C, 57.47; H, 4.83%. IR (KBr disc): $\nu_{C=C}$ 1595 cm^{-1}.

Thermolysis of **2a** *in 1-hexanol*. A solution of *meso*-**2a** (100 mg, 0.30 mmol) in 1-hexanol (2 ml) was refluxed for 3–4 h. After removal of the solvent, the residue was subjected to thin-layer-chromatography on SiO_2 with $CHCl_3$—CCl_4 (1 : 1) to afford *O*-hexyl 2-(phenylvinylphosphinothioyl)ethylphenylphosphinothioate **8** (33 mg, 25%) and *O*-hexyl phenylvinylphosphinothioate **9** (10 mg, 12%) as viscous oil and mobile liquid, respectively.

8: ^{1}H-NMR ($CDCl_3$): δ 0.68–1.00 (m, 3 H, $OC_5H_{10}CH_3$), 1.00–1.76 (m, 8 H, $OCH_2C_4H_8CH_3$), 2.16–2.65 (m, 4 H, PCH_2CH_2P), 3.46–4.30 (m, 2 H, $POCH_2C_5H_{11}$), 5.80–6.60 (m, 3 H, vinyl protons), 7.30–7.63 (m, 6 H, *meta* and *para* protons), and 7.63–8.01 (m, 4 H, *ortho* protons). ^{31}P-NMR ($CDCl_3$): δ_p 40.4 ppm (d, $^3J_{PP}$ = 68.4 Hz, $CH_2{=}CH{-}P(S)Ph{-}$) and 92.6 ppm (d, $^3J_{PP}$ = 68.4 Hz, $C_6H_{13}OP(S)Ph{-}$). In benzene the doublet at δ_p 92.6 ppm separated to two pairs of doublets, indicating that **8** is a diastereomeric mixture. Mass spectrum (70 eV): m/e 436 (M^+, 15%) and 195 ($PhP^+(SH)(CH{=}CH_2)_2$, 100%). High resolution mass spectrum: m/e Found: 436.1199. Calcd. for $C_{22}H_{30}OP_2S_2$: 436.1212.

9: ^{1}H-NMR ($CDCl_3$): δ 0.70–1.06 (m, 3 H, $OC_5H_{10}CH_3$), 1.11–1.83 (m, 8 H, $OCH_2C_4H_8CH_3$), 3.66–4.16 (m, 2 H, $OCH_2C_5H_{11}$), 5.68–6.81 (m, 3 H, vinyl protons), 7.33–7.63 (m, 3 H, *meta* and *para* protons), and 7.73–8.08 (m, 2 H, *ortho* protons). ^{31}P-NMR ($CDCl_3$): δ_p 79.1 ppm. Mass spectrum (70 eV): m/e 268 (M^+, 4.2%) and 184 ($CH_2{=}CH{-}P(S)(OH)Ph^+$, 100%). High resolution mass spectrum: m/e Found: 268.1044. Calcd. for $C_{14}H_{21}OPS$: 268.1049.

Heating *meso*-**2a** in 1-hexanol at 120°C for 3 days gave **8** and **9** in 33 and 12% yields, respectively. When dl-**2a** was used, the quite similar result was obtained. Monitoring by ^{31}P-NMR spectroscopy indicated that isomerization between *meso* and *dl* diastereomers occurred at first and then the products

appeared gradually, whereas **2a** was consumed slowly with keeping equilibrium ratio of *meso* to *dl* isomer. When the reaction was carried out in xylene with equimolar amounts of $ZnBr_2$ and 1-hexanol in sample tube of ^{31}P-NMR, the reaction proceeded even at 80°C for 8 h to give the same NMR pattern as described above, but isomerization of **2a** was not observed. On the contrary, when **2a** was heated in xylene at 100°C with $ZnBr_2$ but without 1-hexanol, only isomerization of **2a** was observed.

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