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OPTICALLY ACTIVE PHOSPHINE OXIDES. 8.[1] SYNTHESIS OF NONSYMMETRICAL 1,2-DIPHOSPHINYLETHENES AND RELATED SYSTEMS

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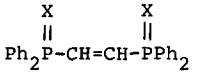
Abstract: The synthesis of the nonsymmetrical and the optically active *trans*-1,2-diphosphinylethenes has been accomplished. The employed addition-elimination route is potentially general and utilizes readily accessible secondary phosphine oxides and tertiary 1-halogenovinyl phosphine oxides. Sterically crowded secondary phosphine oxides afford nonsymmetrical 1,2-diphosphinylethenes directly by heating with the corresponding 1-bromovinyl phosphine oxide in pyridine. For other secondary phosphine oxides a two-step procedure involving corresponding 1-chlorovinyl phosphine oxides is more advantageous. In the syntheses leading to the optically active 1,2-diphosphinylethenes possessing either equivalent or nonequivalent chiral phosphorus centres the novel homochiral (-)-(1-bromovinyl)methylphenylphosphine oxide and (-)-(1-chlorovinyl)methylphenylphosphine oxide have been utilized to afford the very practical self-resolving systems in which one chiral phosphorus centre resolves another. The developed methodology has also been applied to the synthesis of the analogous doubly activated ethenes containing one phosphorus and one sulphur activating group.

INTRODUCTION

Cis- and *trans*-1,2-bis(diphenylphosphino)ethenes 1a as well as their dioxides 1b and other derivatives, enjoy wide application as complexing agents in rare elements extractions[2,3], in electrochemistry as electrode-active compounds[4], in metal complexes as ligands[3,5] and also, as geometrically defined models for



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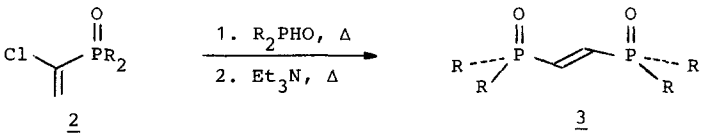
a: X = lone pair
b: X = O
c: X = S

physicochemical studies[6] as well as the highly valuable synthetic intermediates[7]. Recent use of *trans*-1b and *trans*-1c as dienophiles in the preparation of important NORPHOS[8], PHELLANPHOS[9] and NOPAPHOS[9] ligands possessing diphosphine functionality mounted on a rigid carbocyclic skeleton evidently highlights the latter application. In spite of the fact, that the possible use of nonsymmetrically substituted or chiral analogs of 1 would attribute desirable new dimensions of asymmetry and selectivity to the many of the above mentioned applications, other 1,2-diphosphinoethenes and their derivatives have received very little attention.

Only in one report a synthesis of some nonsymmetrical 1,2-diphosphinylethenes has been described[10]; the corresponding optically active systems have not been available. We considered it appropriate therefore, to develop a procedure which would provide nonsymmetrical and nonracemic reagents of this type.

A perusal of the literature revealed only two practical synthetic routes to 1,2-diphosphinoethenes. In one[11], vinylic halogens of either *cis*- or *trans*-1,2-dichloroethene are stereospecifically replaced by two equivalents of alkali metal diarylphosphide to give symmetrical 1,2-diphosphinoethenes. In another one[10], the synthesis of nonsymmetrical *trans*-1,2-diphosphinylethenes is accomplished in a sequence of addition-elimination reactions utilizing secondary phosphine oxides and tertiary 1-chlorovinyl phosphine oxides. Of these, the latter route which is represented in Equation 1 was envisaged by us easily adaptable for the preparation of the optically active systems of type 3 since



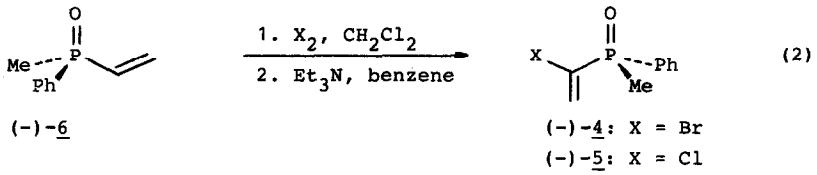
2 3 (1)

either of the substrates for this synthesis could in principle be employed in a nonracemic form. We choose to develop an approach in which the optical activity is introduced to the system with a P-chiral 1-halogenovinyl phosphine oxide rather than with chiral secondary phosphine oxides even though, the latter pool of chiral compounds had a remarkable virtue of having been already available[12]. The chosen approach has however the advantage of allowing the initial centre of chirality of the corresponding P-chiral 1-halogenovinyl phosphine oxide to remain intact throughout the entire synthetic process. Moreover, an access to the previously unknown optically active tertiary 1-halogenovinyl phosphine oxides would also open novel synthetic possibilities through their potentially wide use as chiral Michael-type acceptors or as chiral dienophiles[13]. Herein we report on the preparation of the homochiral (1-bromovinyl)methylphenylphosphine oxide (4) and (1-chlorovinyl)methylphenylphosphine oxide (5) and their use in the synthesis of the first optically active 1,2-diphosphinylethenes possessing either equivalent or nonequivalent chiral phosphorus centres of known configuration. Extention of the developed methodology to the preparation of similar phosphinyl ethenes bearing additional sulphur activating group is also demonstrated. Sulphonyl and sulphinyl activated olefins are also extremely useful intermediates in organic synthesis[14].

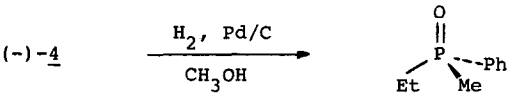
RESULTS AND DISCUSSION

The synthesis of the required chiral 1-halogenovinyl phosphine oxides of high enantiomeric purity was achieved in two simple steps starting from the recently available homochiral methylphenylvinylphosphine oxide (-)-*S*-6[15]. Addition of either bromine or chlorine to (-)-6 followed by treatment of the corresponding adduct with triethylamine to effect elimination of HX, resulted in the straightforward formation of the optically active 4 and 5, respectively, in satisfactory overall yields (Equation 2). Both, the expected *R* configuration and the very high optical purity of these oxides were nicely substantiated by a checking experiment correlating (-)-4 with the optically active ethylmethylphenylphosphine oxide 7 of known configuration. As shown in Equation 3, reductive debromination of the synthesized (-)-4 led directly to (-)-7 for which

the measured $[\alpha]_{589}$ value paralleled very closely the literature value reported for the virtually homochiral (-)-*S*-7[15].



(-)-6 (-)-4: X = Br (-)-5: X = Cl (2)



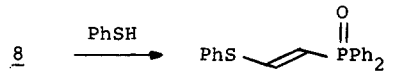
(-)-4 (-)-*S*-7 (3)

Before utilizing either (-)-4 or (-)-5 for the synthesis of optically active 1,2-diphosphinylethenes we have scrutinized comparatively serviceability of the corresponding achiral models 8 and 9, under variety of thermal and base catalyzed conditions and, with emphasis put on the possibility of combining the addition and elimination steps into one preparative operation.

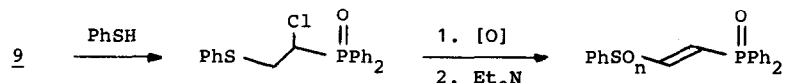
8 9

We have found that heating of equimolar amounts of the bromo oxide 8 and the corresponding secondary phosphine oxide in pyridine does indeed afford the desired *trans*-1,2-diphosphinylethenes directly. This procedure proved to be especially suitable for the preparations involving sterically crowded secondary phosphine oxides. In other cases, the employment of the chloro oxide 9 and the original[10] two step procedure appeared considerably more advantageous. Application of the two procedures for the synthesis of some novel nonsymmetrical *trans*-1,2-diphosphinylethenes is typified in the Table in the first four entries.

It was also possible to extend this methodology to the synthesis of similar doubly activated ethenes containing one phosphorus and one sulphur activating group. For example, reaction of thiophenol with bromo oxide 8 in refluxing pyridine furnished directly *trans*-diphenyl(2-phenylthiovinyl)phosphine oxide 10 (Equation 4), formally securing also an access to the corresponding sulphinyl and sulphonyl compounds 12 and 13, which can be derived from 10 via simple oxidation of sulphur. Alternatively, reaction of thiophenol with the chloro oxide 9 under



8 10 (4)



9 11 12: n = 1 13: n = 2 (5)

practically the same conditions gave the adduct 11, apparently reluctant to eliminate HCl under these conditions. From 11, however, via sequential oxidation-elimination reactions, the sulphoxide 12 and the sulphone 13 were readily obtained in very good overall yields (Equation 5). Adjustment of the oxidation level of sulphur before elimination was conveniently achieved by treatment of 11 with H_2O_2 in MeOH[16] or with H_2O_2/SeO_2 mix in MeOH[17], resulting in the highly selective formation of the corresponding chloro sulphoxide and chloro sulphone, respectively.

TABLE

Synthesis of the Nonsymmetrical and Optically Active 1,2-Diphosphinylethenes and Related Compounds.[a]

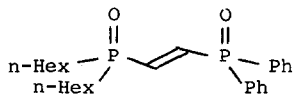
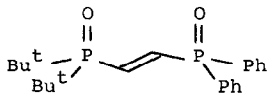
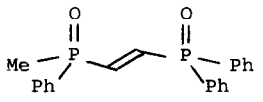
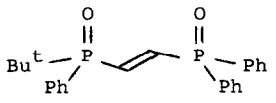
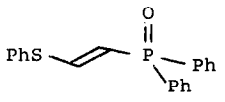
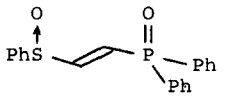
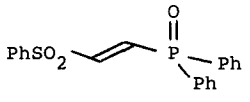
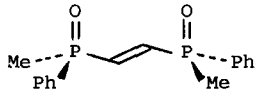
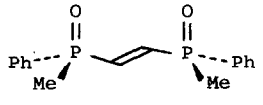
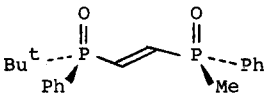
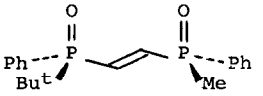
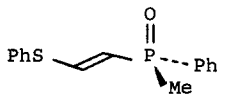
	PRODUCT	Starting oxide	Yield[b] [%]	Mp[c] [°C]	^{31}P NMR δ[d] [ppm]	^{31}P NMR J_{PP} [Hz]
14		9	44.8	122-4	21.8, 38.6	45.0
15		8	52.2(55)	232-6	21.7, 53.0	41.5
16		9	47.8	216-7	21.9, 25.7	50.0
17		8	57.8(77)	203-6	21.9, 38.3	45.1
10		8	53.2(60)	122-3	23.1	
12		9	70.7[e]	175-9	21.9	
13		9	70.8[e]	216-8	21.2	
18a		(-)-5	49.0[e]	214-8	25.48	
18b				278-84	25.54	

TABLE continued

	PRODUCT	Starting oxide	Yield[b] [%]	Mp[c] [°C]	^{31}P NMR δ[d] [ppm]	^{31}P NMR J_{PP} [Hz]
19a		(-)-4	43.6(64)	197-8	38.5, 25.6	44.7
19b				170-2	38.3, 25.4	44.8
20		(-)-4	33.0[f]	70-3	26.2	

[a] The optically active products are depicted in their absolute configurations. [b] The yields given are for the isolated and purified material; in parenthesis are ^{31}P NMR yields. [c] Melting points are uncorrected. [d] In $CHCl_3$ or $CDCl_3$; chemical shift for the P originating from the secondary phosphine oxide is listed as the first. [e] Overall yield calculated on the starting halogenovinyl oxide is given. [f] Isolated after ca. 40% conversion, cf. Experimental.

It thus appeared that both 1-bromovinyl and 1-chlorovinyl phosphine oxides could be advantageously utilized in the preparation of 1,2-diphosphinylethenes and related sulphur containing compounds in a quite complementary way. Our syntheses of the optically active *trans*-1,2-diphosphinylethenes from 4 and 5 followed this conclusion closely.

The synthesis of the optically active *trans*-1,2-bis(methylphenylphosphinyl)-ethene employed, accordingly, secondary methylphenylphosphine oxide and the chloro oxide (-)-5 and was carried out in two steps using toluene as solvent for the addition and pyridine to effect elimination of HCl from the intermediate chloro adduct. The expected diastereomeric *trans*-1,2-bis(methylphenylphosphinyl)-ethenes were obtained as a ~3:5 mixture and were readily separated by short column chromatography on silicagel. Due to the fact that the starting (-)-5 was homochiral and had the known configuration, it was possible to assign the absolute configurations to the two isomers on the basis of the optical rotation measurements alone. Thus, the *S,S* configuration was assigned to the optically active (-)-18a (minor) and, by default, the *R,S* (meso) configuration to the optically inactive 18b (major).

For the exemplary synthesis of the optically active 1,2-diphosphinylethenes possessing two different chiral phosphorus centres we choose secondary *tert*-butylphenylphosphine oxide which, in its reaction with the bromo oxide (-)-4, in pyridine, at 110°C, afforded directly two diastereomeric *trans*-1-(*tert*-butylphenylphosphinyl)-2-(methylphenylphosphinyl)ethenes 19a and 19b in a 47:53 ratio. Formation of only two isomers in this reaction corroborates the original assumption that the configurational homogeneity of the starting (-)-4 would be fully preserved under the conditions applied. The diastereoisomers 19a and 19b were separated by fractional crystallization and were individually identified as the

virtually homochiral (-)-*R,S-trans*-1-(*tert*-butylphenylphosphinyl)-2-(methylphenylphosphinyl)ethene and (-)-*S,S-trans*-1-(*tert*-butylphenylphosphinyl)-2-(methylphenylphosphinyl)ethene, respectively. The absolute sense of chirality of the newly resolved *tert*-butylphenylphosphinyl centres in 19a and 19b was revealed by the chemical correlation involving 19a and the known homochiral (-)-*R,S*-1-(*tert*-butylphenylphosphinyl)-2-(methylphenylphosphinyl)ethane identified unequivocally by means of the single crystal X-ray diffraction technique. This correlation, the correspodning X-ray analysis and discussion of some pertinent diagnostic NMR data have been already reported elsewhere[1].

Finally, the access to the optically active vinyl phosphine oxides bearing vicinal sulphur functionality is exemplified by the straightforward synthesis of (-)-*S*-methylphenyl(2-phenylthiovinyl)phosphine oxide 20 which was obtained from oxide 4 directly, by treatment with thiophenol in refluxing pyridine.

To summarize, the synthesis of the first optically active *trans*-1,2-diphosphinylethenes possessing either equivalent or nonequivalent chiral phosphorus centres has been accomplished. The route employed is potentially general and, importantly, it provides convenient self-resolving systems in which one chiral phosphorus centre is used to resolve another. This methodology offers also convenient access to the interesting doubly activated ethenes containing one phosphorus and one sulphur activating group.

EXPERIMENTAL PART

Melting points and boiling points are uncorrected. All solvents and reagents were purified by standard methods before use. ^{1}H NMR spectra were recorded either on a Tesla BS 487 (80 MHz) or a Bruker MSL-300 (300 MHz) spectrometer. ^{31}P NMR spectra were taken either on the Bruker instrument or on a Jeol-JNM-FX-60 spectrometer operating at 121.4 and 24.3 MHz, respectively. ^{13}C NMR spectra were recorded on the Bruker instrument at 75 MHz. All the ^{1}H and ^{13}C NMR spectra were run on $CDCl_3$ solutions and ^{31}P NMR spectra, on $CDCl_3$ or $CHCl_3$ solutions, unless implied otherwise. Mass spectra were obtained on a LKB-2091 mass spectrometer under 15 and 70 eV electron impact conditions. The optical activity measurements were performed on a Perkin Elmer 241 MC photopolarimeter. Elemental analyses were obtained at Microanalyses Laboratory of the Centre of Molecular and Macromolecular Studies.

Secondary Phosphine Oxides. (*tert*-Butyl)phenylphosphine oxide[18] ($\delta^{31}P$ = 46.81 ppm, $^{1}J_{PH}$ = 454 Hz), di(*tert*-butyl)phosphine oxide[19] ($\delta^{31}P$ = 69.81 ppm, $^{1}J_{PH}$ = 441 Hz) and di(*n*-hexyl)phosphine oxide[20] ($\delta^{31}P$ = 33.99 ppm, $^{1}J_{PH}$ = 444 Hz) were obtained by published procedures. Methylphenylphosphine oxide was conveniently obtained by oxidation of readily available methylphenylphosphine[21], as follows.

A magnetically stirred, water chilled solution of 4.63 g (0.037 mol) in 30 mL of dry deaerated toluene was placed in an atmosphere of pure oxygen (baloon) and was kept under these conditions for at least one week (efficient cooling with water is important during the first few hours of the reaction). As gauged by ^{31}P NMR even after 7 days the toluene solution contained still ca. 4% of unreacted methylphenylphosphine ($\delta^{31}P$ = -71.21 ppm) along with more than 90% of the desired oxide ($\delta^{31}P$ = 18.53 ppm) and only ca. 3% of methylphenylphosphinic acid ($\delta^{31}P$ = 34.24 ppm). We were unable to isolate methylphenylphosphine oxide from this solution in the pure state. Attempted bulb-to-bulb distillation *in vacuo* resulted in disproportionation to the starting phosphine and the methylphenylphosphinic acid. NMR solutions of the oxide in $CDCl_3$ were obtained by replacing toluene with $CDCl_3$ by vacuum-line technique. ^{1}H NMR δ: 1.7 (dd,

J = 4, 14 Hz; 3H), 6.88 - 8.05 (m, 5H), 7.58 (dq, J = 4, 456 Hz; 1H). ^{31}P NMR ($CDCl_3$) δ: 20.2. It is important to prepare the $CDCl_3$ solution of the oxide just before the recording of the spectra because the oxide deteriorates quickly in chlorinated solvents. We used relatively stable crude toluene solution of methylphenylphosphine oxide for preparative purposes. This was usually calibrated by ^{31}P NMR before use.

(-)-*R*-(1-Bromovinyl)methylphenylphosphine Oxide 4. To a solution of 1g (6 mmol) of (-)-methylphenylvinylphosphine oxide 6[15] in 20 mL of CH_2Cl_2 was added dropwise 1 g (6.2 mmol) of bromine and then, progress of the reaction was monitored by TLC (EtOAc - i-PrOH 15:1). When 6 was completely consumed (ca. 2h), to the reaction mixture was added in three portions 1.2 g (12 mmol) of triethylamine. The precipitated hydrochloride was filtered off and the filtrate was washed with water (2 x 10 mL), dried ($MgSO_4$), and evaporated. Kugelrohr distillation of the residue under reduced pressure gave 1.22 g (83%) of pure 4 which solidified in a receiver. Bp 170°C/0.2 Torr, mp 42-4°C, $[\alpha]_{589}$ = -14.9° (c, 3.0, $CHCl_3$). ^{1}H NMR δ: 2.0 (d, J = 13.7 Hz; 3H), 6.48 (dd, J = 2.2, 28.6 Hz; 1H), 6.96 (dd, J = 2.2, 12.2 Hz; 1H), 7.47 - 7.62 (m, 3H), 7.78 - 7.86 (m, 2H). ^{13}C NMR δ: 14.29 (d, J = 78.3 Hz), 126.99 (d, J = 92.1 Hz), 129.33 (d, J = 12.4 Hz), 131.47 (d, J = 106.4 Hz), 131.54 (d, J = 9.6 Hz) 133.09 (bs), 133.83 (d, J = 9.7 Hz). ^{31}P NMR δ: 29.1. MS: m/e 246 (M+1), 244 (M-1), 218, 216, 204, 202, 165 (base), 139, 137, 123.

Low pressure hydrogenation of 150 mg (0.6 mmol) of (-)-4 was performed at room temperature, in CH_3OH, over 3 mol% of Pd/C. After ca. 6 h the reaction mixture was filtered through celite and the filtrate was evaporated to dryness. Kugelrohr distillation of the residue at 200°C/0.3 Torr gave 100 mg (97%) of optically active (-)-*S*-ethylmethylphenylphosphine oxide 7 which was found identical with the one described earlier[15]. $[\alpha]_{589}$ = -24.1° (c, 3.2, CH_3OH), [lit.[15] - 24.4°].

(-)-*R*-(1-Chlorovinyl)methylphenylphosphine Oxide 5. To a solution of 2.49 g (0.015 mol) of (-)-*S*-6[15] in 25 mL of CH_2Cl_2 was introduced slowly (through a dry-ice condenser) 2 g (0.03 mol) of chlorine. The reaction mixture was kept at room temperature (water bath) for ca. 2 h. Excess of chlorine and CH_2Cl_2 were removed under reduced pressure and the crude adduct was dissolved again in 25 mL of $CHCl_3$ and treated dropwise with 9.11 g (0.09 mol) of triethylamine at room temperature. After the addition was completed (ca. 1 h) the chloroform was replaced with benzene and the mixture was filtered and evaporated to give crude product which after repeated Kugelrohr distillations under reduced pressure yielded 2.7 g (90%) of pure (-)-5. Bp 115°C/0.01 Torr, mp 49-51°C, $[\alpha]_{589}$ = -97.3° (c, 4.6, $CHCl_3$). ^{1}H NMR δ: 1.9 (d, J = 13.7 Hz, 3H), 6.14 (dd, J = 1.1, 27.1 Hz; 1H), 6.46 (dd, J = 1.1, 11.0 Hz; 1H), 7.42 - 7.52 (m, 3H), 7.72 - 7.79 (m, 2H). ^{13}C NMR δ: 14.06 (d, J = 77.7 Hz), 129.3 (d, J = 12.2 Hz), 129.35 (d, J = 11.9 Hz), 131.3 (d, J = 9.6 Hz), 131,36 (d, J = 106 Hz), 133.06, 136.7 (d, J = 100.6 Hz). ^{31}P NMR δ: 28.55. MS, m/e 202 (M+2), 200 (M+), 165, 158, 139 (base), 123, 77, 51, 47.

(1-Bromovinyl)diphenylphosphine Oxide 8. This compound was prepared from diphenylvinylphosphine oxide[22] as described previously[23]. Overall yield: 63%. Mp 63-9°C (lit.[23] 68-70°C). ^{1}H NMR δ: 6.61 (dd, J = 2.1, 30.2 Hz; 1H), 6.82 (dd, J = 2.1, 12.6 Hz; 1H), 7.44 - 7.6 (m, 6H), 7.74 - 7.83 (m, 4H). ^{13}C NMR δ: 126.16 (d, J = 95.3 Hz), 129.19 (d, J = 12.4 Hz), 130.5 (one arm of an overlapped doublet), 132.9 (d, J = 10 Hz), 133.17 (d, J = 1.8 Hz), 135.9 (d, J = 10.4 Hz). ^{31}P NMR δ: 26.73.

(1-Chlorovinyl)diphenylphosphine Oxide 9. This compound was similarly prepared from diphenylvinylphosphine oxide[22] as described previously[23]. Overall yield: 75%. Mp 80-1°C (lit.[23] 76-7°C). ^{1}H NMR δ: 6.3 (dd, J = 1.8, 28.2 Hz; 1H), 6.46 (dd, J = 1.8, 11.3 Hz; 1H), 7.4 - 7.6 (m, 6H), 7.7 - 7.85 (m, 4H). ^{13}C NMR δ: 129.22 (d, J = 12.6 Hz), 130.6 (one arm of the overlapped doublet), 131.6 (d, J = 12.9 Hz), 132.85 (d, J = 10.2 Hz), 133.23, 135.86 (d, J = 103.4 Hz). ^{31}P NMR δ: 25.4.

Trans-1-(di-*n*-hexylphosphinyl)-2-(diphenylphosphinyl)ethene 14. A solution of 1.33 g (5 mmol) of 9 and 1.09 g (5 mmol) of di(*n*-hexyl)phosphine oxide in 10 mL of toluene was heated to reflux under argon for 12 h. After this time ^{31}P NMR monitoring indicated almost complete conversion of the substrates. Toluene was then replaced with pyridine and the reflux was continued for additional 14 h. After evaporation of pyridine the residue was dissolved in chloroform, then washed twice with water and dried over anhydrous magnesium sulphate. Removal of the solvent left crude 14 which was recrystallized from heptane to give 1 g (44.8%) of analytically pure sample. ^{1}H NMR δ: 0.82 (t, J = 6.9 Hz; 3H), 1.1 - 1.95 (m, 20H), 7.1 - 7.8 (m, 12H). ^{13}C NMR δ: 22.16 (d, J = 3.6 Hz), 22.92, 29.79 (d, J = 68.8 Hz), 31.19 (d, J = 13.8 Hz), 31.86, 129.41 (d, J = 12.3 Hz), 131.55 (one arm of an overlapped doublet), 131.81 (d, J = 10.1 Hz), 132.91, 142.69 (d, J = 88.5 Hz), 142.95 (d, J = 69.1 Hz). Anal.calcd for $C_{26}H_{38}O_2P_2$: C, 70.24; H, 8.61; P, 13.93. Found: C, 70.3; H, 8.63; P, 13.65.

Trans-1-(di-*tert*-butylphosphinyl)-2-(diphenylphosphinyl)ethene 15. A solution of 0.162 g (1 mmol) of di(*tert*-butyl)phosphine oxide and 0.307 g (1 mmol) of 8 in 2.5 mL of pyridine was sealed under argon in a glass ampoule and heated to 150-160°C for 25 h. Evaporation of pyridine from the resulting mixture gave a solid residue which was subsequently dissolved in chloroform, washed twice with water and dried over anhydrous magnesium sulphate. Removal of the solvent provided crude 15 which was recrystallized from toluene-heptane mixture to afford 203 mg (51.5%) of pure 15. (This compound can also be prepared in comparable yields from 9, either by heating as above or by the two-step procedure). ^{1}H NMR δ: 1.24 (d, J = 14 Hz; 18H), 7.4 - 7.7 (m, 12H). ^{13}C NMR δ: 27.25, 35.82 (d, J = 62.1 Hz), 129.46 (d, J = 12.1 Hz), 131.82 (d, J = 9.5 Hz), 132-87, 133.37 (one arm of an overlapped doublet), 140.59 (d, J = 64.4 Hz), 143.22 (d, J = 89 Hz). MS, m/e 388 (M+), 275 (base), 221, 149, 73, 57.

Trans-1-(methylphenylphosphinyl)-2-(diphenylphosphinyl)ethene 16. A solution of 119 mg (0.85 mmol) of methylphenylphosphine oxide in toluene (vide supra) was mixed under argon with a solution of 211 mg (0.8 mmol) of 9 in 1.5 mL of deaerated toluene and the resulting mixture was heated to reflux for 8 h. Subsequent replacement of toluene with triethylamine (or pyridine) and heating of the new solution at 90°C for 12 h completed the overall transformation. Excess of amine was then evaporated and the residue was dissolved in chloroform, washed twice with water and dried over anhydrous magnesium sulphate. Evaporation of the solvent gave crude 16 which was recrystallized from toluene to give 140 mg (47.8%) of pure sample. [A direct synthesis of 16 by heating of the two substrates in pyridine at reflux for 16 h gave considerably lower yields (21%)]. ^{1}H NMR δ: 1.74 (d, J = 13.3 Hz; 3H), 7.28-7.67 (m, 17H). ^{13}C NMR δ: 17.3 (d, J = 74.4 Hz), 129.52 (multiplet of broad overlapping lines), 130.71 (d, J = 9.5 Hz), 131.87 (d, J = 9.7 Hz), 132.01 (d, J = 105.9 Hz), 132.97 (br s), 140,99 (d, J = 87.6 Hz), 143.58 (d, J = 83.7 Hz). MS, m/e 366 (M^+), 227 (base), 201, 165, 139, 51, 47.

Trans-1-(*tert*-butylphenylphosphinyl)-2-(diphenylphosphinyl)ethene 17. A solution of 153 mg (0.5 mmol) of 8 and 91 mg (0.5 mmol) of (*tert*-butyl)phenylphosphine oxide in 2 mL of pyridine was heated at reflux, under argon, for 7 h. To the resulting hot solution was added large excess of water (ca. 90 mL) and the precipitated 17 was collected by filtration and dried in a dessicator over P_2O_5. Recrystallization from toluene gave 119 mg (57.8%) of pure 17. Analogous synthesis in which 9 was used in lieu of 8 required much longer heating for completion (28 h) but gave comparable yield of 17. ^{1}H NMR δ: 1.17 (d, J = 15.4 Hz; 9H), 7.36 - 8.0 (m, 17H). ^{13}C NMR δ: 24.79, 33.84 (d, J = 72.3 Hz), 129.05 (d, J = 10.9 Hz), 129.38 (d, J = 13 Hz), 129.5 (d, J = 11.8 Hz), 131.9 - 132.5 (complex groups of signals with several overlapping lines), 132.89 (br s), 139.47 (d, J = 76.5 Hz), 144.03 (d, J = 87.3 Hz), signals of Ph-P ipso carbons were obscured. MS, m/e 408 (M^+), 351, 275 (base), 201, 183, 133, 77, 47.

Trans-1-(diphenylphosphinyl)-2-(phenylthio)ethene 10. A solution of 5 g (0.0163 mol) of 8 and 1.79 g (0.0163 mol) of thiophenol in 30 mL of pyridine was heated to reflux for 46 h. After removal of pyridine under reduced pressure the crude product was dissolved in 50 mL of chloroform, washed with water (2 x 25 mL) and dried over anhydrous magnesium sulphate. Removal of the solvent gave solid residue which, after passing through a short column of silicagel using chloroform-ethyl acetate (4:5) as eluent, was recrystallized from ethyl acetate to give 2.9 g (53.2%) of pure 10. ^{1}H NMR δ: 6.05 (br dd, J = 16.5, 20.1 Hz; 1H), 7.28 - 7.47 (m, 12H), 7.56 - 7.8 (m, 4H). ^{13}C NMR δ: 116.4 (d, J = 103.2 Hz), 129.15 (d, 12.2 Hz), 129.24, 130.25, 131.37, 131.8 (d, J = 10 Hz), 132.4 (br s), 133.54, 133.68 (d, J = 106.3 Hz), 148.82 (d, J = 6.2 Hz). Anal.calcd for $C_{20}H_{17}OPS$: C, 71.14; H, 5.1; P, 9.21; S, 9.53. Found: C, 71.19; H, 5.26; P, 9.09; S, 9.47.

[(1-Chloro-2-phenylthio)ethyl]diphenylphosphine Oxide 11. To a solution of 5 g (19 mmol) of 9 in 10 mL of pyridine was added 4 g (38 mmol) of thiophenol and the mixture was kept at 90°C for 16 h. After complete removal of pyridine and excess of thiophenol under reduced pressure, the residue was recrystallized from ethyl acetate-heptane to give 6.74 g (95.2%) of pure 11. Mp 138-141°C. ^{1}H NMR δ: 3.05 (ddd, J = 4.9, 11.3, 14.6 Hz; 1H), 3.73 (ddd, J = 2.3, 4.8, 14.6 Hz; 1H), 4.45 (ddd, J = 2.3, 4.2, 11.3 Hz; 1H), 7.18 - 7.36 (m, 5H), 7.39 - 7.55 (m, 6H), 7.66 - 7.75 (m, 2H), 7.82 - 7.88 (m, 2H). ^{13}C NMR δ: 37.37, 54.35 (d, J = 67.8 Hz), 127.85, 129.2 (d, J = 12 Hz), 129.46 (d, J = 12 Hz), 129.87, 131.5, 132.03 (d, J = 9.2 Hz), 132.14 (d, J = 8.9 Hz), 133.2 - 133.3 (four br lines), 134.61, (signals for Ph-P ipso carbons were obscured). ^{31}P NMR δ: 30.47. MS, m/e 372 (M^+), 337 (base), 228, 201, 109, 77.

Trans-1-(diphenylphosphinyl)-2-(phenylsulphinyl)ethene 12. To a magnetically stirred solution of 4 g (10.7 mmol) of 11 in 25 mL of methanol was added 2.5 g of 30% hydrogen peroxide and the reaction mixture was kept at room temperature by means of a water bath. After 24 h additional 2.5 g of 30% hydrogen peroxide was added and stirring at room temperature was continued till the ^{31}P NMR monitoring of the reaction indicated total consumption of 11 (72 h). 50 mL of water were then added and the resulting solution was extracted with chloroform (3 x 100 mL). The extracts were combined, dried over anhydrous magnesium sulphate, and evaporated to yield 4 g (96%) of crude chloro sulphoxide which was used as such for the subsequent elimination. [A small purified sample of this material, mp 157-9°C, δ^{31}P: 30.79, gave correct analysis: calcd for $C_{20}H_{18}O_2PSCl$: C, 61.77; H, 4.67; P, 7.97; S, 8.24; Cl, 9.11. Found: C, 61.4; H, 4.87; P, 8.07; S, 8.27;

Cl, 9.03, and correct ^{1}H NMR δ: 3.03 (ddd, J = 5.1, 12.4, 13.4 Hz; 1H), 3.17 (ddd, J = 2.3, 3.9, 13.4 Hz; 1H), 5.05 (dt, J = 2.3, 12.4 Hz; 1H), 7.41 - 7.62 (m, 11H), 7.7 - 7.85 (m, 4H)].

In 10 mL of chloroform was dissolved 2.6 g of triethylamine and 2.1 g of the crude chloro sulphoxide and the resulting solution was heated to reflux for 3 h. Additional 30 mL of chloroform were then added and the mixture was washed with water (2 x 50 mL) and dried over anhydrous magnesium sulphate. Evaporation of the solvent gave crude 12 which was finally purified by crystallization from ethyl acetate-diethyl ether. 12: 1.48 g (74.3%). ^{1}H NMR δ: 7.4 (dd, J = 15.9, 22.7 Hz, 1H), 7.41 - 7.75 (m, 16H). ^{13}C NMR δ: 125.33, 126.7 (d, J = 91.6 Hz), 129.4 (d, J = 12.5 Hz), 130.42, 131.73 (d, J = 13 Hz), 131.8 (d, J = 10.2 Hz), 132.44, 132.98, 154.02, (signals for Ph-P ipso carbons were obscured). MS, m/e 352 (M^+), 336, 250, 202, 197, 77 (base).

Trans-1-(diphenylphosphinyl)-2-(phenylsulphonyl)ethene 13. To a water cooled solution of 2 g (5 mmol) of 11 in 10 mL of methanol was added with stirring 0.57 g (5.14 mmol) of selenium dioxide and 0.7 mL of 30% hydrogen peroxide. The resulting white slurry soon became thick and after ca. 40 min. methanol was replaced with chloroform, and the resulting solution was then washed with water (2 x 40 mL) and finally dried over anhydrous magnesium sulphate. Removal of the solvent gave 2.07 g of the chloro sulphone as white crystals. Mp 170-6°C, δ^{31}P: 30.77, ^{1}H NMR δ: 3.53 (ddd, J = 3, 11.2, 15.1 Hz; 1H), 3.84 (ddd, J = 1.5, 7.2, 15.1 Hz, 1H), 4.99 (ddd, J = 1.5, 6, 11.2 Hz; 1H), 7.48 - 7.77 (m, 9H), 7.8 - 7.94 (m, 6H). MS, m/e 405 (M+1), 228, 227, 201 (base), 77.

The chloro sulphone (1.8 g, 4.45 mmol) was then dissolved in chloroform (30 mL) and treated with 5 equivalents of triethylamine, at room temperature, for 1 h, to yield the vinyl sulphone 13 which was isolated as described above. Recrystallization from chloroform-carbon tetrachloride gave 1.22 g (74.4%) of pure 13. ^{1}H NMR δ: 7.3 (t, J = 16.1 Hz, 1H), 7.46 - 7.69 (m, 14H), 7.86 - 7.9 (m, 2H). ^{13}C NMR δ: 128.93, 129.6 (d, J = 12.5 Hz), 130.21, 130.3 (one arm of an overlapped doublet), 131.85 (d, J = 10.1 Hz), 133.38, 134.92, 135.45 (d, J = 81.1 Hz), 138.97, 146.26. Anal. calcd for $C_{20}H_{17}O_3PS$: C, 65.2; H, 4.65; P, 8.41; S, 8.70. Found: C, 65.2; H, 4.77; P, 8.41; S, 8.92.

Trans-1,2-bis(methylphenylphosphinyl)ethenes 18. A solution of 2.3 g (16.4 mmol) of methylphenylphosphine oxide in toluene (vide supra) was mixed under argon with a solution of 2.8 g (14 mmol) of (-)-5 in 10 mL of deaerated toluene and the resulting mixture was heated to reflux for 16 h. Toluene was then replaced with 20 mL of pyridine and the new solution was again heated to reflux for 5 h. Removal of pyridine under reduced pressure left a solid residue which was dissolved in 25 mL of chloroform, washed with water (2 x 15 mL) and dried over anhydrous magnesium sulphate. Evaporation of chloroform gave crude 18 as a mixture of two diastereoisomers in ca. 3:5 ratio (TLC). The isomers were separated by column chromatography on silicagel using chloroform-ethanol (10:1) as eluent and gave the pure compounds in 49% total yield. (-)-*S*,*S*-18a: 0.78 g (18.4%). $[\alpha]_{589}$ = -53.6° (c, 2, $CHCl_3$). ^{1}H NMR δ (second order spectrum): 1.78 (filled-in doublet, line separation 13.2 Hz, 6H), 7.28 (t, $J_{AX} + J_{BX}$ = 50 Hz, 2H), 7.35 - 7.49 (m, 6H), 7.56 - 7.64 (m, 4H). ^{13}C NMR δ (second order spectrum, only the central lines of multiplet signals are listed): 16.83, 128.97, 130.11, 132.24, 141.9. MS, m/e 304 (M^+), 289, 227, 165 (base), 139, 83, 77, 47. *R*,*S*-18b: 1.3 g (30.6%). ^{1}H NMR δ (second order spectrum): 1.71 (filled-in doublet, line separation 13.2 Hz, 6H), 7.27 (t, $J_{AX} + J_{BX}$ = 50 Hz, 2H), 7.41 - 7.53 (m, 6H), 7.62 - 7.71 (m, 4H). ^{13}C NMR δ (second order spectrum, only the central

lines of multiplet signals are listed): 16.4, 128.82, 129.92, 132.1, 141.62. MS, m/e 304 (M^+), 289, 227, 165 (base), 139, 83, 77, 47.

Trans-1-(*tert*-butylphenylphosphinyl)-2-(methylphenylphosphinyl)ethenes 19. A solution of 0.68 g (2.8 mmol) of (-)-4 and 0.51 g (2.8 mmol) of (*tert*-butyl)-phenylphosphine oxide in 6 mL of pyridine was heated to reflux under argon for 12 h. After removal of pyridine under reduced pressure the residue was passed through a short column of silicagel using chloroform-methanol (20:1) as eluent to give 0.62 g (64%) of crude 19, as ca. 1:1 mixture of two diastereoisomers. These were separated by preparative TLC using the aforementioned eluent and multiple development technique which furnished the two pure components in 43.6% total yield. (-)-*R*,*S*-19a: 0.22 g (23%). $[\alpha]_{589}$ = -76.6° (c, 2.5, $CHCl_3$). ^1H NMR δ: 1.09 (d, J = 15.5 Hz, 9H), 1.79 (d, J = 13.3 Hz, 3H), 7.3 - 7.47 (m, 7H), 7.5 - 7.79 (m, 5H). ^{13}C NMR δ: 16.89 (d, J = 74.2 Hz), 24.12, 33.08 (d, J = 72.3 Hz), 128.2 - 132.5 (three groups of overlapping signals too complex to assign in detail), 132.0 (d, J = 103.5 Hz), 137.6 (d, J = 74.64), 144.7 (d, J = 84.32). MS, m/e 347 (M+1), 290, 275 (base), 271, 215, 139, 123. (-)-*S*,*S*-19b: 0.2 g (20.6%). $[\alpha]_{589}$ = -0.9° (c, 1.2, $CHCl_3$). ^1H NMR δ: 1.04 (d, J = 15.5 Hz, 9H), 1.73 (d, J = 13.3 Hz, 3H), 7.41 - 7.62 (m, 7H), 7.67 - 7.77 (m, 5H). ^{13}C NMR δ: 16.6 (d, J = 74.4 Hz), 24.1, 33.1 (d, J = 71.9 Hz), 128.46 - 133.2 (three groups of overlapping signals too complex to assign in detail), 144.87 (d, J = 85.3 Hz); another wide doublet at ca. 138 δ was also discerned but could not be assigned precisely. MS, m/e 346 (M^+), 290, 275 (base), 271, 215, 139, 125.

Trans-1-(methylphenylphosphinyl)-2-(phenylthio)ethene 20. A solution of 0.268 g (1.1 mmol) of (-)-4 and 0.24 g (2.2 mmol) of thiophenol in 3 mL of pyridine was heated to reflux and progress of the reaction was monitored by ^{31}P NMR. A spectrum taken directly on the reaction mixture after 45 h of heating indicated complete consumption of 4 and the presence of three main (75% by integration) phosphorus containing products corresponding to signals at 19.44, 32.03 and 32.53 δ. To identify these products which were tentatively assigned as the expected 20 and the two diastereomeric intermediate bromo adducts, respectively, the reaction was worked-up at this stage. Thus, after evaporation of pyridine under reduced pressure, the crude reaction mixture was subjected to chromatography on a short column of silicagel using ethyl acetate as eluent. Two main fractions were collected of which the larger one (0.187 g, 47.9%) was indeed confirmed to be a 3:2 mixture of the two corresponding bromo adducts: ^1H NMR δ: 1.77 (d, J = 13 Hz) major, and 1.79 (d, J = 12.8 Hz) minor, (3H); 2.73 (ddd, J = 7.4, 10.5, 17.8 Hz) and 3.09 (m) and 3,35 (ddd, J = 4, 10.5, 12.2 Hz) and 3.43 (m) and 3.81 (ddd, J = 4, 7.4, 14.1 Hz), (3H total); 6.91 - 7.78 (m, 10H). ^{31}P NMR δ: 39.04 (the two lines coincided in $CDCl_3$). The remaining minor fraction was additionally purified by distillation in Kugelrohr at 230°C/0.01 Torr and eventually identified as (-)-20: 99 mg (33%). $[\alpha]_{589}$ = -66.9° (c, 1.2, $CHCl_3$). ^1H NMR δ: 1.73 (d, J = 13.2 Hz, 3H), 5.86 (dd, J = 16.5, 21.5 Hz, 1H), 7.32 - 7.54 (m, 9H), 7.64 - 7.72 (m, 2H). As indicated by the presence of two additional low intensity signals at δ 1.89 (d, J = 13.4 Hz) and 5.96 (dd, J = 12.2, 19.8 Hz) in this spectrum, the analyzed sample contained ca. 12% (by integration) of the corresponding cis isomer. ^{13}C NMR δ: 17.37 (d, J = 75.8 Hz), 117.25 (d, J = 99.8 Hz), 128.68 (d, J = 11.9 Hz), 129.0, 129.62, 130.0 (d, J = 9.6 Hz), 130.85, 130.93, 131.68, 132.95, 134.1 (d, J = 102.5 Hz), 146.8 (d, J = 5.2 Hz). MS, m/e 274 (M^+), 197 (base), 165, 149, 140, 73.

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