

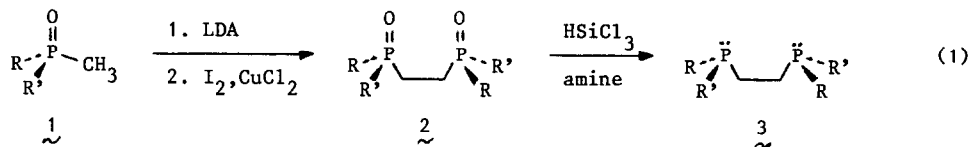
OPTICALLY ACTIVE PHOSPHINE OXIDES. 4.<sup>1</sup>  
 A STRAIGHTFORWARD SYNTHESIS OF P-CHIRAL 1,2-DIPHOSPHINOYLETHANES.

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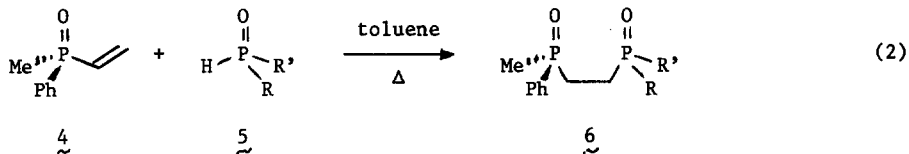
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**Abstract:** The title compounds possessing either one or two homochiral phosphorus centres are conveniently prepared via non-catalyzed addition of secondary phosphine oxides to an optically active vinyl phosphine oxide.

The use of asymmetric catalysis for the production of optically active compounds is rapidly gaining a position of prominence in synthetic practice.<sup>2</sup> Widely employed are organometallic catalysts in which ligands are used as the chiral auxiliaries.<sup>3</sup> Optically active 1,2-diphosphinoethanes possessing either backbone or phosphorus chirality rank among the most efficient ligands of this type.<sup>4</sup> Spectacular laboratory and industrial performance of diPAMP (3; R=*o*-anisyl, R'=Ph) in some rhodium catalysed asymmetric hydrogenations has early indicated the great practical value of such ligands.<sup>5</sup> A search for other similarly efficient P-chiral 1,2-diphosphinoethane ligands has however been stymied by the lack of convenient methods for their preparation.<sup>4</sup> The only developed route to these compounds involving oxidative coupling<sup>6</sup> of a chiral methylphosphine oxide (Equation 1), is laborious and requires separate synthesis of the starting phosphine oxide of high optical purity for each individual entry.<sup>6,7</sup>



One practical alternative for assembling chiral structures 2 is suggested by the known facility with which secondary phosphine oxides add across the double bond of vinyl phosphine oxides.<sup>8</sup> We wish to demonstrate in this communication that optically active 1,2-diphosphinoylethanes of type 2, as well as a variety of others possessing two non-equivalent phosphorus atoms, can easily be prepared in such a way from a single homochiral precursor, i.e., (-)-(S)-methylphenylvinylphosphine oxide 4<sup>9</sup> (Equation 2).



Selected examples are collected in the Table. They include systems containing one and two chiral phosphorus centres arising from 4 and symmetrical and non-symmetrical 5, respectively.

The latter systems are especially noteworthy. Compounds 6e-l constitute a unique collection of *self-resolving*<sup>10</sup> chiral di(tertiary phosphine) oxides in which the chirality of one phosphorus centre is used to resolve another chiral phosphorus atom. The two homochiral diastereomers thus obtained can be separated readily by fractional crystallization or by chromatography, as demonstrated for 6i,j and 6k,l, respectively. These compounds constitute also the first examples of the optically active 1,2-diphosphinoylethanes possessing two non-equivalent asymmetric phosphorus atoms.

The experimental procedure for the synthesis of diphosphinoylethanes 6 is straightforward. Heating of a toluene solution of the two reactants in equimolar amounts (5-8 mL of toluene for 1 mmol of 4 and 5) at reflux for 2-4 h leads to the formation of the desired product in high yield. The product crystallizes out of the reaction mixture upon cooling to room temperature and is isolated in the pure state by simple filtration.

All the 1,2-diphosphinoylethanes 6a-j are adequately characterized by MS, <sup>1</sup>H NMR and <sup>31</sup>P NMR. Most of them gave typical AB-type <sup>31</sup>P NMR spectra at 121.4 MHz and revealed large three bond P-P coupling. The observed <sup>3</sup>J<sub>P-P</sub> values of 36-51 Hz suggest that the compounds prefer antiperiplanar conformations in solution. Values of 35-45 Hz were previously found to correspond to ca. 170° P-C-C-P dihedral angle (in phosphole dimers oxides).<sup>11</sup> For *exo*, *endo*-2,3-bis(diphenylphosphinoyl)-norbornane (dihedral P-C-C-P angle close to 120°) coupling of only 9.8 Hz was observed.<sup>12</sup> At lower field the spectra of 6c and 6d consisted only of a singlet as if the two P atoms in these compounds were equivalent. It appears therefore, that the substitution of H by an aryl in the P-CH<sub>3</sub> group causes only negligible shift of the phosphorus nucleus.<sup>13</sup> Interestingly, this phenomenon is observed only in tertiary phosphine oxides. The corresponding shift by an α-phenyl substituent is typically several parts per million for secondary phosphine oxides<sup>14</sup> and is well over +10 ppm for tertiary phosphines.<sup>15</sup>

To summarize, the presented method for the synthesis of P-chiral 1,2-diphosphinoylethanes is simple and general. Both reactants can be considerably diversified in structure.<sup>16</sup> Use of the recently described (+)-(S)-(o-anisyl)phenylvinylphosphine oxide<sup>16b</sup> and secondary (o-anisyl)phenylphosphine oxide in the proposed manner offers, for example, a convenient access to diPAMP dioxide (2; R=o-anisyl, R'=Ph).

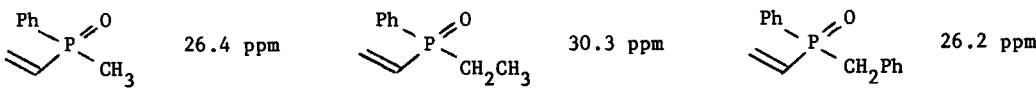

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TABLE. Synthesis of P-chiral 1,2-diphosphinoethanes **6**

Diphosphinoethane <b>6</b>	Yield <sup>a</sup> [%]	Mp <sup>b</sup> [°C]	[α] <sub>D</sub> <sup>c</sup> [deg]	Absolute configur.	<sup>31</sup> P NMR <sup>d</sup>	
					δ [ppm]	J <sub>P-P</sub> [Hz]
<b>6a</b> 	73	134-5	-22.8	S	37.1, 48.0	46.6
<b>6b<sup>e</sup></b> 	69	126-8	-3.2	S	38.9, 59.8	36.6
<b>6c</b> 	89	183-5	-29.2	S	37.5, 43.0	46.4
<b>6d</b> 	89	186-7	-50.8	S	37.5, 31.8	51.3
<b>6e, f<sup>f</sup></b> 	92	163-86	-18.8	S, (R,S)	37.8, 38.4	48.4
<b>6g, h<sup>f</sup></b> 	85	200-4 <sup>g</sup>	-27.2	S, (R,S)	37.8, 38.4	48.8
<b>6i<sup>h</sup></b> 	38	172-3	-11.0	S, R <sup>i</sup>	37.8, 50.9	44.4
<b>6j<sup>h</sup></b> 	33	174-6	+0.9	S,S	38.1, 50.6	44.4
<b>6k<sup>j</sup></b> 	41	235-7	0	S,R	37.9 <sup>k</sup>	
<b>6l<sup>j</sup></b> 	37	204-6	-59.6	S,S	37.9 <sup>k</sup>	

<sup>a</sup> <sup>31</sup>P NMR monitoring of the reactions indicated 92-100% conversion of both reactants in each case. The yields given are for the isolated (crystallized) material. <sup>b</sup> Melting points are uncorrected. <sup>c</sup> In CHCl<sub>3</sub>. <sup>d</sup> In CHCl<sub>3</sub>; chemical shifts of the MePhP(O)-phosphorus is listed as the first. <sup>e</sup> Synthesis carried out in a sealed tube, 180°C, 15 h. <sup>f</sup> Not separated; the data given are for the mixture of isomers. <sup>g</sup> Another part of the sample melted at 230-6°C. <sup>h</sup> Separated by fractional crystallization from benzene. <sup>i</sup> Assignment based on the X-Ray analysis; to be published elsewhere. <sup>j</sup> Separated by preparative TLC with CHCl<sub>3</sub>-CH<sub>3</sub>OH 20:1 as eluent. <sup>k</sup> Signals of **6k** and **6l** are at the same δ for individual compounds but they are separated by 0.1 ppm for a mixture.

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- By contrast, similar substitution by a Me shifts phosphorus downfield by about 4 ppm. Cf.  $^{31}\text{P}$  NMR ( $\text{CHCl}_3$ )  $\delta$ :  

- Cf.  $^{31}\text{P}$  NMR (benzene)  $\delta$ :  

- Cf.  $^{31}\text{P}$  NMR (neat)  $\delta$ : 1-methyl phospholane, -32.0 ppm; 1-benzyl phospholane, -14.4 ppm. Breen, J.J.; Engel, J.F.; Myers, D.K.; Quin, L.D. *Phosphorus* 1972, *2*, 55.
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