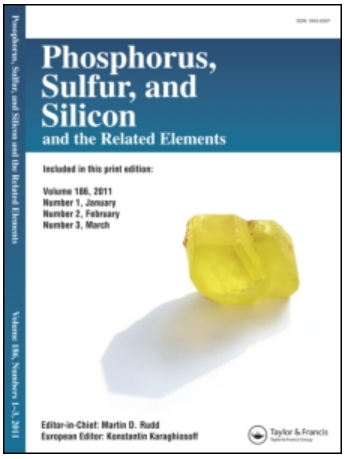

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STERIC CONTROL OF THE P-CHIRAL GROUP IN GRIGNARD ADDITION TO THE CARBONYL GROUP OF α - KETOPHOSPHINE OXIDE

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STERIC CONTROL OF THE P-CHIRAL GROUP IN GRIGNARD ADDITION TO THE CARBONYL GROUP OF α-KETOPHOSPHINE OXIDE

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1,2-Asymmetric inductions in Grignard addition to the carbonyl group of α-keto P-chiral phosphine oxides have been investigated. The favoured reaction product erythro-, **6**, is thermodynamically less stable than the threo isomer. This seems to be the first stereochemical evidence of the reversible character of reaction addition of sec-phosphine oxides to the carbonyl group.

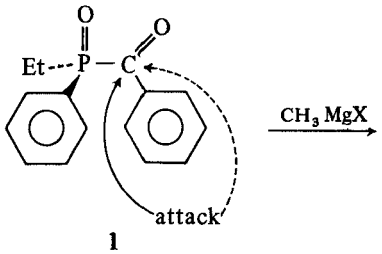
P-Chiral organic phosphorus compounds have been shown to be effective chirality transfer agents, either acting as reagents[1a–f] or as ligands in metal complexes used as homogeneous catalysts.[2]

The stereoselectivity of Grignard addition to carbonyl compounds which contain asymmetric centre led to the formulation of Cram's rule and Prelog's rule. These rules emphasize that the effective size of the groups substituted at the asymmetric carbon atom is the principal factor governing the approach of the reagent.[3]

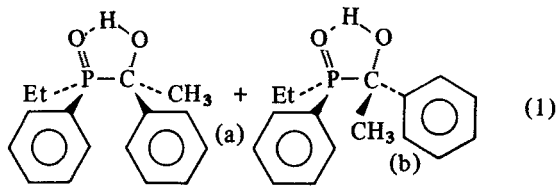
In our previous paper[1f] we investigated chirality transfer to carbon atom in Horner-Emmons synthesis involving P-chiral reagent. Now, we wish to report 1,2-asymmetric induction in Grignard addition to the carbonyl group of α-keto P-chiral phosphine oxides. It seemed likely that one of the substituents (P=O) at the chiral phosphorus atom of the α-keto phosphine oxide could co-ordinate with the magnesium of the Grignard reagent giving a transition state of different conformation from that of the ground state.

We have prepared the following compounds: (±)benzoylethylphenylphosphine oxide $C_6H_5(C_2H_5)P(O)COC_6H_5$, **1**, m.p. 82–3° (64% yield); (±)ethylphenylpivalonoylphosphine oxide $C_6H_5(C_2H_5)P(O)COC(CH_3)_3$, **2**, b.p. 89–91/0.01 mmHg (51% yield); (±)methylbenzoylphenylphosphinate $C_6H_5(CH_3O)P(O)COC_6H_5$, **3**, m.p. 77–8° (lit.[9] m.p. 78.5°) (67% yield); (±)methylphenylpivalonoylphosphinate $C_6H_5(CH_3O)P(O)COC(CH_3)_3$, **4**, b.p. 86–7°/0.2 mmHg (56% yield) and acetylethylphenylphosphine oxide $C_6H_5(C_2H_5)P(O)COCH_3$, **5**, b.p. 108–113°/0.05 mmHg (41% yield).

The ketone, **1**, was treated by methylmagnesium iodide in ether at various temperatures (−70° to +30°C) affording a mixture of erythro-, **6**, and threo-, **6**, (1-hydroxy-1-phenylethyl)ethylphenylphosphine oxides, m.p. 106–13° (85% yield).



1



(1)

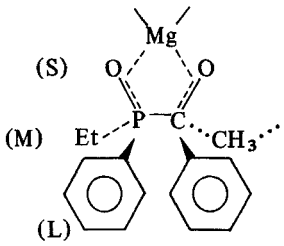
erythro- **6** threo- **6**

The proportion of isomers was determined by NMR. The signals due to methyl groups CH_3 (a) and CH_3 (b) appear as doublets and have different chemical shifts and coupling constant ($^3J_{PH}$).

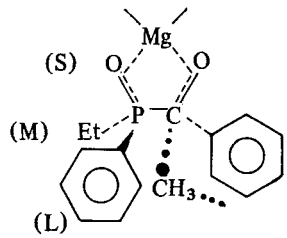
The mixture of the stereomeric oxides, **6**, was separated by crystallization into pure isomers erythro-, **6** (m.p. 117–8°; CH_3 (a) 1.89 ppm) and threo, **6** (m.p. 137–8°; CH_3 (b) 1.58 ppm). The high field signal of the methyl group in the threo-, **6**, isomer,

is due to the long-range shielding effects associated with the benzene ring[4] bonded to the phosphorus atom. Such an effect is very likely since the coupling[10] of P=O with the aromatic π-system, and the rigid conformation of the molecule, due to the strong hydrogen bond, stabilizes the position of CH_3 (b) group in the shielded regions.

The ratio of erythro-, **6**, to threo-, **6**, diastereoisomers was found to be 70 : 30 irrespective of the reaction temperature. The configuration of the dominant product is easily explained in the classical way. Although spectroscopic and dipole moment measurements[11] have shown that cisoidal conformations of α-ketophosphine oxides are highly unfavourable, the reaction mechanism involving cisoidal transition states in the addition of Grignard reagent to **1** should be favoured according to Cram's model



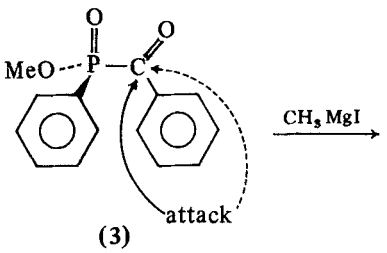
(2)



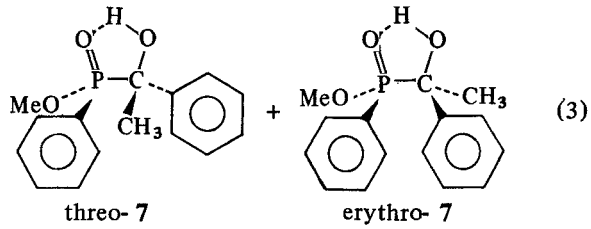
Since the oxygen atom of the P=O group can form complexes with the magnesium atom like those formed by other groups.[5] The transition state (Scheme 2) creating the erythro-, **6**, isomer is reached via attack of the Grignard on the carbonyl carbon of (1) from the side carrying the ethyl (M) group. The threo-, **6**, isomer is formed by attack from the other side [phenyl (L) group].

It was of interest to see to what extent the size of the group on the chiral phosphorus atom determined the steric course of the reactions. We therefore used methylbenzoylphenylphosphinate, **3**, as substrate, because in this case one can expect some electronic effect due to the methoxy group.

We characterized the product as a mixture of threo-**7**, and erythro-, **7**, methyl(1-hydroxy-1-phenylethyl)phenylphosphinate by NMR. Threo-, **7**, predominated in the mixture (57 : 43) indicating that attack from the less sterically hindered side (methoxy group) is unfavourable, presumably because of electron lone pair repulsion on the nucleophilic reagent.



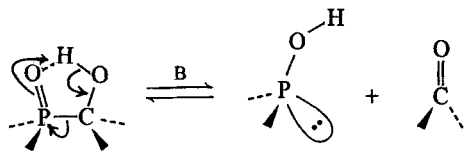
(3)



threo- **7** erythro- **7**

(3)

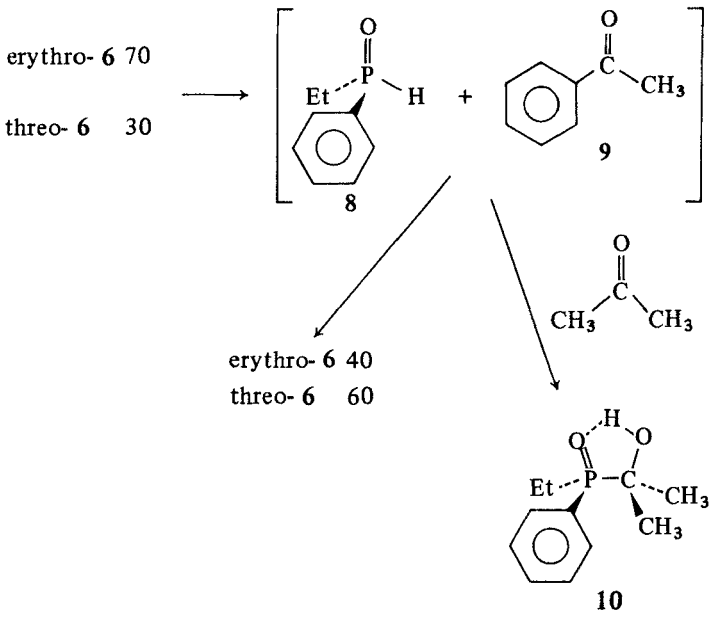
We strongly believe that the ratio of erythro-, **6**: threo-, **6**, isomers is kinetically controlled and does not depend on temperature of the reaction, and that the predominant product erythro-, **6**, should be thermodynamically less stable. We therefore attempted to verify this suggestion. It is known that α-hydroxyphosphine oxides and related compounds decompose to secondary phosphine oxides and carbonyl compounds.[6]



(4)

On the other hand it has been found[7] that secondary phosphine oxides add to carbonyl groups giving α-hydroxyphosphine oxides. In both reactions base catalysis is usually applied. From these observations one can conclude that the decomposition and the addition should be reversible processes.

We expected that the erythro-, **6**, isomer would undergo C–P bond cleavage faster than the threo-, **6**, isomer. In fact, the mixture of erythro-, **6** : threo-, **6**, isomers (70 : 30) heated with excess of acetone became considerably enriched in threo-, **6**, isomer. Acetone captures sec-phosphine oxide, **8**, affording the known[8] (1-hydroxy-1-methylethyl)ethylphenylphosphine oxide, **10**



(5)

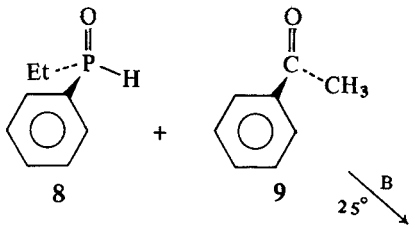
The formation of acetophenone, **9**, in the reaction mixture is easily observed by GLC monitoring.

The adduct of **8** to acetone was separated and purified. The NMR spectrum of the α-hydroxyphosphine oxide, **10**, shows two doublets due to diastereotopic methyl groups. The difference in chemical shifts, $\Delta\delta = 0.3$ ppm, is equal to the difference observed for the methyl groups of the erythro-, **6**, and threo-, **6**, isomers. Also, the differences between the coupling constant $^3J_{PH}$ of the diastereotopic groups in **10** and the methyl groups CH_3 (a), CH_3 (b) of erythro-, **6**, and threo-, **6**, respectively, are very similar.

To find the thermodynamically controlled ratio of oxides, **6**, a mixture of erythro-, **6**, and threo-, **6**, from the Grignard addition (70 : 30) was heated at 90°C with an excess of acetophenone. The NMR spectrum of the crude product showed one doublet at high field, which had been earlier attributed to the threo-, **6**, isomer. The doublet at low field corresponding to the erythro-, **6**, isomer was not observed. Thus, under the conditions of thermodynamic control the threo-, **6**, isomer is formed exclusively. The stereochemical results of equilibration and the experiment described by Scheme (5) confirmed the thermodynamic stability of the threo-, **6**.

In further work we attempted to determine the steric course of the additions of sec-phosphine oxide, **8**, to acetophenone, **9**.

Treating the oxide, **8**, with an equimolar amount of ketone, **9**, and sodium ethanolate (cat.) in ethanol at 25°C we obtained a mixture of erythro-, **6**, and threo-, **9** (70 : 30); this was rather unexpected. However, when the reaction was carried out at 75° the exclusive formation of the pure threo-, **6**, isomer was observed. It appears that at 25°C the addition to form **6** is not totally reversible.



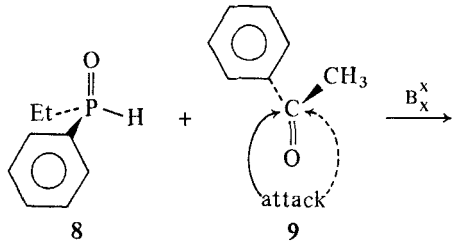
erythro- **6** 70
threo- **6** 30

(6)

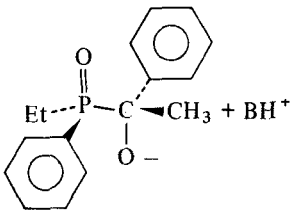
In contrast to the results discussed above, the addition of methylphenylphosphinite, **11**, to acetophenone, **9**, under conditions of thermodynamic control, gave an exact 50 : 50 mixture of threo-, **7**, and erythro-, **7**, strengthening our argument that the product of reaction (3) was formed under kinetic control (57 : 43).

Our naïve attempt to explain the results of kinetic control in the addition to form **6** at 25°C is based on the assumption that approach of substrates in the corresponding transition states is transoidal with respect to the P=O and C=O dipoles. In the case

leading to the erythro-, **6**, isomer the nonbonding interaction should be much weaker.



8 **9**



(7)

erythro- **6**

The cisoidal P=O and C=O approach of substrates leading to the formation of the transition states having the weakest nonbonding interaction should favour the threo-, **6**, isomer.

In order to strengthen our argument, we treated acetoxy phosphine oxide $C_6H_5(C_2H_5)P(O)COCH_3$, **5**, with phenyl magnesium bromide, except for the formation of the threo-, **6**, isomer which should be kinetically and thermodynamically favoured. Unfortunately the addition failed.

ACKNOWLEDGEMENT

We are very much indebted to Professor Jan Michalski for his kind interest and wish to thank the Polish Academy of Sciences for partial support of this work.

EXPERIMENTAL

M. ps. were determined on a Büchi melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Infracord Model 137 Spectrometer. NMR spectra were taken on Tesla BC-487c or JEOL C-60 HL spectrometers using 5–10% solutions with TMS as an internal standard. Chemical shifts are given in ppm. Mass spectra were obtained on a LKB GCMS model 2091 with 70 eV ionization potential.

All compounds containing asymmetric atoms are racemic.

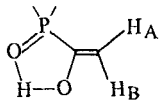
Benzoylethylphenylphosphine oxide (**1**). To a stirred solution of benzoyl chloride (10.8 g; 0.076 mole) under N_2, ethylethylphenylphosphinite (15.8 g; 0.087 mole) was added at temperature below 35°C, and the resulting mixture stirred at room temperature for 2 hr. The oil which slowly solidified was purified by recrystallization from THF/n-hexane to give (**1**) as slightly yellow prisms (12.6 g; 64% yield) m.p. 82–3°; IR (KBr): 3040, 2950, 1638, 1600, 1580, 1450, 1440, 1225, 1180, 1030 cm^{-1}; NMR (CCl_4): δ 1.14 (d.t., $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 18.0 Hz, 3H), δ 1.9–2.60 (m., 2H), δ 7.25–7.50 (m., 6H), δ 7.65–7.95 (m., 2H), δ 8.35–8.55 (m., 2H); {H} ^{31}P δ 1.14 (t., $^3J_{HH}$ = 7.5 Hz, 3H), δ 2.23 (q., $^3J_{HH}$ = 7.5 Hz, 2H); MS: m/e = 258 (Found: C. 69.86; H, 5.93; P, 11.80. $C_{15}H_{15}O_2P$ requires: C, 69.76; H, 5.81; P, 12.00%).

Ethylphenylpyvalonolylphosphine oxide (**2**). The reaction was carried out using the procedure described above with pivaloyl chloride (12.7 g; 0.105 mole) and ethylethylphenylphosphinite (22.9 g; 0.126 mole). The crude product (**2**) (12.6 g; 51% yield) was obtained by distillation b.p. 89–90°/0.01 mm; IR (film): 3040, 2950, 1675, 1590, 1480, 1460, 1440, 1390, 1365, 1190, 1040 cm^{-1}; NMR ($CDCl_3$): δ 1.24 (s., 9H), δ 1.75–2.45 (m., 2H), δ 7.25–8.0 (m., 5H); MS: m/e = 238 (Found: C, 65.42; H, 8.04; P, 13.18. $C_{13}H_{19}O_2P$ requires: C, 65.54; H, 7.98; P, 13.02%).

Methylbenzoylphenylphosphinate (**3**). The reaction was carried out using the procedure described above with benzoyl chloride (16.8 g; 0.12 mole) and dimethylphenylphosphonite (22.1 g; 0.13 mole). The resulting product slowly crystallized (**3**), slightly yellow prisms (THF/pentan) (20.8 g; 67% yield) m.p. 77-8°; IR (KBr): 3040, 2950, 1655, 1595, 1580, 1450, 1440, 1225, 1020 cm^{-1}; NMR (CCl_4): δ 3.80 (d., $^3J_{PH}$ = 11.0 Hz), δ 7.35–7.60 (m., 6H), δ 7.64–8.05 (m., 2H), δ 8.33–8.50 (m., 2H); MS: m/e = 260 (Found: C, 64.45; H, 5.01; P, 11.65. Calc. for $C_{14}H_{13}O_3P$: C, 64.61; H, 5.00; P, 11.91%).

Methylphenylpivaloylphosphinate (**4**). The reaction was carried out using the procedure described above with pivaloyl chloride (16.0 g; 0.135 mole) and dimethylphenylphosphonite (27.5 g; 0.162 mole). The crude product was purified by distillation, (**4**), (18.2 g; 56.1% yield) b.p. 86–7°/0.2 mm; IR (film): 3040, 2950, 1680, 1590, 1480, 1460, 1440, 1390, 1360, 1225, 1030 cm^{-1}; NMR (CCl_4): δ 1.24 (s., 9H), δ 3.67 (d., $^3J_{PH}$ = 11.5 Hz); δ 7.35–7.55 (m., 3H), δ 7.6–7.9 (m., 2H): MS: m/e = 240 (Found: C, 60.15; H, 7.13; P, 13.08. $C_{12}H_{17}O_3P$ requires: C, 60.00; H, 7.08; P, 12.91%.

Acetylethylphenylphosphine oxide (**5**). The reaction was carried out using the procedure described above with acetyl chloride (25.8 g; 0.329 mole) and ethylethylphenylphosphinite (12.0 g; 0.066 mole) at –5°. The product was distilled, (**5**), (5.3 g; 41% yield), b.p. 108–113°/0.05 mm; IR (film): 3075, 3000, 2950, 1768, 1630, 1440, 1220, 1170, 1030 cm^{-1}. NMR (CCl_4): δ 1.1 (d.t., $^3J_{PH}$ = 17 Hz, $^3J_{HH}$ = 7.5 Hz, 3H),* δ 2.06 (s., 3H), δ 1.8–2.4 (m., 2H) δ 5.82 (d.d., $^2J_{H_AH_B}$ = 2.0 Hz, $^3J_{PH_B}$ = 36.0 Hz, 1H)*



δ 5.92 (d.d., $^2J_{H_AH_B}$ = 2.0 Hz, $^3J_{PH_A}$ = 1.0 Hz 1H),* δ 7.2–7.55 (m., 3H) δ 7.6–8.0 (m., 2H); (CD_3OD): δ 1.15 (d.t., $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ 7.5 Hz, 3H), δ 2.1 (s., 3H), δ 5.83 (d.d., $^2J_{H_AH_B}$ = 2.5 Hz, $^3J_{PH_B}$ = 21.0 Hz, 1H), δ 6.05 (d.d., $^2J_{H_AH_B}$ = 2.5 Hz, $^3J_{PH_A}$ = 4.0 Hz, 1H), δ 7.35–7.65 (m., 3H), δ 7.7–8.0 (m., 2H); MS: m/e = 196 (Found: C, 61.00; H, 6.80; P, 15.59 Colc for $C_{10}H_{13}O_2P$: C, 61.22; H, 6.64; P, 15.81.

* Signals due to keto and enol forms (80 : 20).

(1-Hydroxy-1-phenylethyl)ethylphenylphosphine oxides (**6**). To a solution of benzoylethylphenylphosphine oxide (**1**) (2.0 g; 0.0077 mole) in ether (200 ml), methyl magnesium iodide (2.03 g; 0.012 mole) in ether (80 ml), was added dropwise at −10°. Stirring was continued for 2 hr. A solution of ammonium chloride in water (50%) was added slowly to the cooled mixture. The ether layers were separated and the water layer was extracted (3 x 100 ml of ether). The combined organic extracts were dried ($MgSO_4$) and concentrated to afford colourless crystals (1.8 g; 85%), m.p. 106–113°. The product was a mixture of erythro-, **6**, and threo-, **6**, isomers.* The NMR Spectra of the crude product showed a ca, 7 : 3 predominance of the erythro isomer (Found: C, 70.07; H, 6.93; P, 11.31. $C_{16}H_{19}O_2P$ requires: C, 69.98; H, 7.01; P. 11.20%).The mixture was recrystallized from ethanol to give the pure isomers erythro-, **6**, m.p. 117–18° (from ethanol/ether 1 : 1); IR (KBr): 3180, 2950, 1590, 1495, 1450, 1160 cm^{-1}; NMR (CD_3OD): δ 1.05 (d.t., $^3J_{PH}$ = 16 Hz, $^3J_{HH}$ = 8 Hz, 3H), δ 1.5–1.75 (m., 2H), δ 1.89 (d., $^3J_{PH}$ = 13.0 Hz, 3H), δ 7.0–7.8 (m., 10H); MS: m/e = 274; threo-, **6**, m.p. 137–38° (from ethanol) m.p. 142–3° (from methyl cyanide); IR (KBr): 3280, 2950, 1590, 1500, 1450, 1160 cm^{-1}. NMR (CD_3OD): δ 0.78 (d.t., $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 8 Hz 3H), δ 1.2–1.4 (m., 2H), π 1.58 (d. $^3J_{PH}$ = 14.0 Hz 3H), δ 7.25–8.1 (m., 10H).

Methyl-(1-hydroxy-1-phenylethyl)phenylphosphinate (**7**). To a solution of methylbenzoylphenylphosphinate (**3**) (1.56 g; 0.006 mole), in ether (200 ml), methyl magnesium iodide (1.5 g 0.009 mole), in ether (80 ml), was added dropwise at 0°. Stirring was continued for 2 hr. A solution of ammonium chloride in water (50%) was slowly added. The water layer was extracted with ether (3 x 100 ml). The combined etheral solutions were dried ($MgSO_4$) and concentrated to yield colourless crystals (0.94 g; 60%), m.p. 118–25°. MS: m/e = 276; The product was a mixture of erythro-, **7**, and threo-, **7**, isomers. The NMR Spectra of the crude product showed a 43 : 57 predominance of the threo isomer (Found: C, 65.08; H, 6.30; P, 11.07. $C_{15}H_{17}O_3P$ requires: C, 65.21; H, 6.16; P, 11.23%). The mixture was recrystallized from methanol to give the pure isomers: erythro-, **7**, m.p. 128–9° (from methanol/ethyl acetate 1 : 1); IR (KBr): 3230, 2950, 1595, 1500, 1450, 1190, 1030 cm^{-1}; NMR (piridine d_5): δ 2.08 (d., $^3J_{P-H}$ = 14.0 Hz, 3H), δ 3.66 (d., $^3J_{P-H}$ = 10.5 Hz., 3H), δ 7.10–7.55 (m., 10H); threo-, **7**, m.p. 147–8° (from methyl cyanide); IR (KBr): 3370, 2950, 1595, 1500, 1450, 1200, 1040 cm^{-1}; NMR (piridine D_6): δ 1.98 (d., $^3J_{PH}$ = 15 Hz, 3H), δ 3.48 (d., $^3J_{PH}$ = 10.5 Hz, 3H), δ 7.20–7.65 (m., 10H).

(1-Hydroxy-1-methylethyl)ethylphenylphosphine oxide (**10**). The mixture of erythro-, **6**, and threo-, **6** (70 : 30) 2 g was heated with excess acetone (12 g) for 12 hr.† The solvent was evaporated and the NMR spectrum (CD_3OD) of the crude product showed signals attributed to the threo-, **6**, isomer and to **10**. The pure **10** was recrystallized from ethanol to give colourless crystals (0.85 g, 55%) m.p. 125–26°; (lit.[9] 125–6°); IR (KBr) 3200, 2950, 1595, 1440, 1385, 1370, 1155 cm^{-1}; NMR (CD_3OD): δ1.05 (d.t., $^3J_{PH}$ = 17 Hz. $^3J_{HH}$ = 7.5 Hz, 3H), δ 1.18 (d., $^3J_{PH}$ = 13.8 Hz, 3H), δ 1.48 (d., $^3J_{PH}$ = 13 Hz, 3H), δ 1.95–2.60 (m., 2H), δ 7.35–7.65 (m., 3H) δ 7.65–7.95 (m., 2H) (Found: C, 61.95; H, 7.89; P, 14.49. Calc for $C_{11}H_{17}O_2P$: C, 61.79; H, 8.01; P, 14.62). The mother-liquors were examined by GLC and the presence of acetophenon was confirmed.

Equilibration of erythro-, **6** *and threo-,* **6** (3 : 1), 5 ml of acetophenone and 100 ml of benzene were added. The mixture was heated at 90°C for 6 hr. The excess of acetophenone and benzene were removed under reduced pressure. The resulting solid was analysed by NMR, and shown to be the pure threo-, **6**, isomer m.p. 129–32°. The IR and NMR spectra were identical to those described above for the pure threo-, **6**, isomer.

Addition of sec-(ethylphenyl) phosphine oxide to acetophenone. To a mixture of sec-(ethylphenyl) phosphine oxide, **8**, (2.20 g; 0.014 mole) and acetophenone, **9** (1.74 g; 0.014 mole), a solution of sodium ethoxide (0.01 g Na) in ethanol (2 ml) was slowly added dropwise and the resulting mixture stirred at 25° for 2 hr. The suspension was treated with petroleum ether (10 ml) and filtered off (3.15 g, 80%) m.p. 108–115°. The NMR Spectra of the crude product showed a 70 : 30 predominance of the erythro-, **6**, isomer. When the temperature of the reaction was raised to 75° (6 hr), the product was the pure threo-, **6**, isomer.

Addition of methyl hydrogenphenylphosphonate to acetophenone. To a mixture of hydrogenphenylphosphonate, **11**, (4.0 g; 0.025 mole) and acetophenone, **9** (3.2 g; 0.025 mole), a solution of sodium methoxide (0.01 g Na) in methanol (2 ml) was slowly dropped into and stirred at 25°C. The first crystals appeared after 1/2 hr and stirring was continued for an additional 1.5 hr. After treatment with petroleum ether (10 ml), the crude product methyl (1-hydroxy-1-phenylethyl)phenylphosphinate, **7**, was filtered off (6.96 g; 96%). The ratio of diastereoisomers, threo-, **7**, and erythro-, **7**, was determined by NMR integration and shown to be exactly 50 : 50.

* Yield and erythro/threo ratio were independent of the temperature range (−70 to +30°) of the reaction.

† When the heating was stopped after 6 hr. the NMR Spectrum of crude product evidently showed the erythro-, **6**, threo-, **6**, and phosphine oxide, **10**, mixture (20, 30 and 50% respectively).

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