

SYNTHESIS OF SOME PHOSPHINES CONTAINING CHIRAL SUBSTITUENTS*

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Twelve new amino-, alkoxy-, and tertiary phosphines containing chiral substituents are reported. These were prepared by transformation of optically active natural compounds such as camphor, galactose, malic and tartaric acids.

The synthesis of optically active compounds by reaction of prochiral substrates catalysed by transition metal complexes containing chiral ligands attracts increasing attention (for reviews see¹⁻³). In most of the studies, synthetically not readily available tertiary phosphines with chiral phosphorus atom were employed as the ligands. Only few examples of the phosphines bearing chiral substituents have so far been reported, such as {[[(2,2-dimethyl-1,3-dioxolane-4,5-diyl)-bismethylene]bis(diphenylphosphine)} (diop)⁴, neomenthyldiphenylphosphine⁵ and menthyldiphenylphosphine⁶.

For an intended study of asymmetric hydrosilylation we have prepared a series of chiral phosphines of the latter type (compounds *I–XIII*) derived from optically active natural substances such as α -hydroxy acids, terpenes and monosaccharides. Their synthesis is described in the present work and their effectiveness in asymmetric hydrosilylation of ketones will be reported in the subsequent communication⁷.

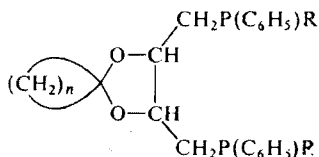
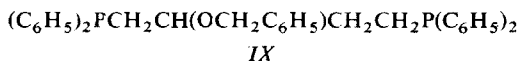
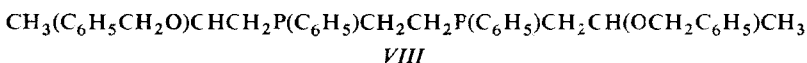
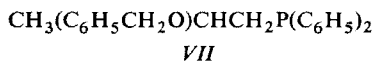
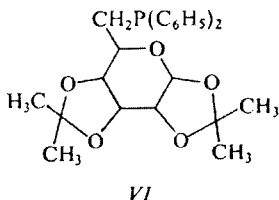
Aminophosphines *I* and *II* were obtained by reaction of the appropriate chiral secondary amines in aprotic solvents with the corresponding chlorophosphines in the presence of triethylamine as a hydrogen chloride acceptor. Alkoxyphosphines *III* and *IV* were prepared from chiral alcohols in a similar way.

The chiral precursors chosen allowed to prepare tertiary phosphines *V–XIII* by the uniform procedure. The introduction of the phosphine group in the last step of the synthesis was realized by means of the organometallic reagent. The phosphides were obtained by the two methods: *a*) by the cleavage of the P–Cl bond of the chlorophosphines R^1R^2PCl ($R^1, R^2 = \text{aryl, alkyl}$) with lithium in tetrahydrofuran⁸ (phosphines *V–VII, IX–XI* and *XIII*) and *b*) by the cleavage of the

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-isopropylidene-1,4-bis(4'-tolylsulphonyl)-L-threitol by its transformation to the corresponding 2,3-diol followed by the conversion of the latter compound to the cyclohexylidene derivative by azeotropic ketalization with cyclohexanone. For preparing this phosphine we have used an alternative route based on the reaction of the diethyl tartrate with 1,1-dimethoxycyclohexane which proved to be more convenient. In this case, each of the subsequent steps gives better results compared to the synthesis from the isopropylidene derivative. In addition, because of the greater ability to crystallize, phosphine X was obtained also in the higher total yield compared to the diop (44% vs 16% calculated with respect to tartaric acid).

We have attempted to utilize the reaction of a prochiral phosphide with a chiral alkylating reagent to prepare the phosphines with the chirality also on phosphorus atom (compounds VIII, XI and XII). In this case, a significant asymmetric synthesis could not be expected to take place on the phosphorus atom¹³. Nevertheless, providing that the diastereoisomers formed can be separated, the compounds with chirality on phosphorus could be obtained which otherwise are prepared with difficulty and by multistep synthesis¹⁴. However, none of the above derivatives of this type was crystalline substance and the separation by thin-layer chromatography has so far been unsuccessful.



- X, n = 5, R = C₆H₅
 XI, n = 5, R = CH₂C₆H₅
 XII, n = 5, R = cyclo-C₆H₁₁
 XIII, n = 4, R = C₆H₅

EXPERIMENTAL

Melting points were determined with a Kofler hot plate microscope and are uncorrected. Optical rotations of the samples were measured on Perkin Elmer 141 or Polamat A (Zeiss, Jena, GDR) polarimeter.

Aminophosphines

(*S*)-2-Methyl-1-piperidyl)diphenylphosphine (I). A solution of 19.4 g (88 mmol) of chlorodiphenylphosphine in 20 ml of benzene was added dropwise to 8 g (80 mmol) of (+)-2-methylpiperidine¹⁵ ($[\alpha]_{\text{D}}^{20} + 36.8^\circ$ (*in substantia*); recorded¹⁶ $[\alpha]_{\text{D}}^{20} + 36.5^\circ$ (*in substantia*)) and 9.72 g (96 mmol) of triethylamine dissolved in 20 ml of benzene at temperature below 20°C. The mixture was stirred at room temperature for 3 h, filtered, the solvent was partially removed by distillation and the residue distilled under reduced pressure to give 12 g (53%) of an oil; b.p. 178 to 179°C/0.5 Torr, $[\alpha]_{\text{D}}^{20} - 17.2^\circ$ (*c* 10, tetrahydrofuran). For C₁₈H₂₂NP (283.4) calculated: 76.30% C, 7.82% H; found: 76.65% C, 7.64% H.

Bis((*R*)-2-methyl-1-piperidyl)phenylphosphine (II). To a solution of 7 g (70 mmol) of (–)-2-methylpiperidine ($[\alpha]_{\text{D}}^{20} - 20.35^\circ$ (*in substantia*)) and 8.5 g (84 mmol) of triethylamine in 50 ml of benzene, 6.9 g (38.5 mmol) of dichloro(phenyl)phosphine dissolved in 15 ml of benzene were added dropwise at 10°C under stirring which was continued for another 3 h (room temperature), the hydrochloride of the base was filtered-off and the filtrate was worked-up similarly as in the preceding case to afford 4 g (38%) of the product, b.p. 100–105°C/0.5 Torr, $[\alpha]_{\text{D}}^{20} - 1.62^\circ$ (*c* 10, tetrahydrofuran). For C₁₈H₂₉N₂P (304.4) calculated: 71.02% C, 9.60% H; found: 71.38% C, 9.78% H.

Alkoxyphosphines

Dimethoxy(phenyl)phosphine (III). To a solution of 57.6 g (0.37 mol) of (–)-menthol and 29.8 ml (0.37 mol) of pyridine in 250 ml of benzene, 25 ml (0.194 mol) of dichloro(phenyl)phosphine were added during 1 h under stirring and cooling the reaction mixture to 0°C. The mixture was then allowed to stand overnight, the pyridine hydrochloride removed by filtration and the residue was cooled to 0°C. The crystalline product obtained had m.p. 66–68°C, $[\alpha]_{\text{D}}^{20} - 56.49^\circ$ (*c* 2.62, chloroform). For C₂₆H₄₁O₂P₂ (418.6) calculated: 74.60% C, 10.35% H; found: 74.54% C, 10.40% H.

[(*S*)-1-(ethoxycarbonyl)ethoxy]diphenylphosphine (IV). A solution of 17.9 ml (0.1 mol) of chlorodiphenylphosphine in 100 ml of light petroleum was added dropwise during 0.5 h under stirring to 11.8 g (0.1 mol) of ethyl (*S*)-lactate and 8.1 ml (0.1 mol) of pyridine dissolved in 100 ml of the same solvent. The reaction mixture was set aside for 12 h at room temperature. After the pyridine hydrochloride and solvent removal, the residual viscous liquid was purified by molecular distillation at 10^{–5} Torr (bath temperature 100°C) to yield 17 g (57%) of a liquid, $[\alpha]_{\text{D}}^{20} - 38.8^\circ$ (*c* 10.3, diethyl ether). For C₁₇H₁₉O₃P (302.3) calculated: 67.54% C, 6.34% H; found: 67.32% C, 6.61% H.

Tertiary Phosphines

1,2,2-Trimethyl-1(*R*,3*S*)-1,3-bis(diphenylphosphino)methylcyclopentane (V). A solution of lithium diphenylphosphide (0.19 mol) in 400 ml of tetrahydrofuran was added to 30 g (0.06 mol) of 1,3-O-bis(4'-tolylsulphonyl)ester of 1(*R*,3*S*)-1,3-bis(hydroxymethyl)-1,2,2-trimethylcyclopentane (m.p. 149–149.6°C, $[\alpha]_{\text{D}}^{20} + 19.56^\circ$ (*c* 0.302, chloroform); recorded¹⁷ $[\alpha]_{\text{D}}^{20} + 14.28^\circ$, m.p. 147°C)

and the mixture was refluxed for 5.5 h, the solvent was removed by distillation under reduced pressure, the residue was dissolved in 150 ml of water and 150 ml of benzene, stirred for 30 min, the organic layer was separated, dried over magnesium sulphate and filtered. After solvent removal, the residual oily liquid was purified by chromatography on silica gel (acetone-hexane (1 : 10) as an eluent); $[\alpha]_{546}^{20} + 78.7^\circ$ (*c* 5.16 benzene). For $C_{34}H_{38}P_2$ (507.6) calculated: 80.45% C, 7.35% H; found: 80.12% C, 7.06% H.

6-Diphenylphosphino-6-deoxo-1,2,3,4-diisopropylidene-D-galactose (VI). A solution of 11 g (27 mmol) of 1,2,3,4-diisopropylidene-6-O-(4'-tolylsulphonyl)-D-galactose (m.p. 88–91°C, $[\alpha]_{546}^{20} - 63.25^\circ$ (*c* 2.06, 1,1,2,2-tetrachloroethane); reported¹⁸ m.p. 91–92°C, $[\alpha]_{546}^{20} - 64.7^\circ$ (1,1,2,2-tetrachloroethane)) in 30 ml of tetrahydrofuran was added dropwise during 30 min to a stirred solution of lithium diphenylphosphide (30 mmol) in the same solvent (50 ml) and the reaction mixture was stirred at room temperature for 4 h. After the work-up and threefold crystallization from ethanol, the product (2.86 g, 28%) was obtained which melted at 131.5–132°C; $[\alpha]_{546}^{20} - 101.4^\circ$ (*c* 1.52, chloroform). For $C_{24}H_{29}O_5P$ (428.5) calculated: 67.28% C, 6.82% H; found: 67.20% C, 6.76% H.

(S)-2-Benzyloxy-1-diphenylphosphinopropane (VII). A solution of 91 g (0.77 mol) of ethyl (*S*)-lactate and 400 g (2.34 mol) of benzyl bromide in 300 ml of diethyl ether was warmed up to 50°C and then silver(I) oxide (266 g, 1.15 mol) was added portionwise such that the temperature did not raise above 55°C. Then the mixture was stirred at room temperature for 2 h, cooled to 0°C, filtered and the filtration cake was washed with the ether. Combined filtrates were freed of the solvent on a vacuum rotatory evaporator and the residue was distilled through a 30 cm-adiabatic distillation column filled with wire spirals, yielding 120 g of a liquid boiling at 109–113°C/2.5 Torr; $\alpha_{546}^{20} - 65^\circ$ (*l* = 1, *in substantia*). A portion of this fraction (104 g, *c*. 0.5 mol) was dissolved in 200 ml of diethyl ether and the solution was added dropwise to 25 g (0.66 mol) of lithium aluminium hydride suspended in 250 ml of the ether. Then the mixture was refluxed for 0.5 h, the excess hydride decomposed in the usual way, the salts filtered-off and extracted with the ether. Combined filtrates and extracts were freed of the solvent and the residue was distilled under reduced pressure to give 59.1 g (80%) of the product boiling at 116–117°C/2 Torr; $\alpha_{546}^{20} + 31.4^\circ$ (*l* = 1, *in substantia*), n_D^{20} 1.5151. As found by gas chromatography, (+)-(*S*)-2-benzyloxy-1-chloropropane was contaminated by *c*. 5% of unidentified lower boiling substance. For $C_{10}H_{14}O_2$ (166.2) calculated: 72.26% C, 8.49% H; found: 71.90% C, 8.20% H. A solution of 76.5 g (0.28 mol) of triphenylphosphine and 43.8 g (0.26 mol) of (+)-2-benzyloxy-1-propanol in 530 ml of tetrachloromethane was refluxed for 2.5 g. After cooling to room temperature, 265 ml of pentane were added and the precipitated triphenylphosphine oxide was removed by filtration. Distillation of the filtrate afforded a fraction boiling at 108–118°C/7 Torr which was fractionated to yield 37.4 g (79%) of (+)-(*S*)-2-benzyloxy-1-chloropropane; b.p. 110–112°C/7 Torr, $[\alpha]_{546}^{20} + 11.09^\circ$ (*c* 1.41, chloroform). For $C_{10}H_{13}ClO$ (184.7) calculated: 65.64% C, 7.10% H; found: 65.66% C, 7.14% H.

A solution of 10 g (45 mmol) of (*S*)-2-benzyloxy-1-chloropropane in 25 ml of tetrahydrofuran was added dropwise to a stirred tetrahydrofuran solution (80 ml) of lithium diphenylphosphide (48 mmol). The mixture was stirred at room temperature for 15 min and worked-up. The residual oil was purified by molecular distillation under a pressure of 10^{-5} Torr (bath temperature 150°C) and the purity of the phosphine VII was verified by thin-layer chromatography (Silufol, acetone-hexane (1 : 8)); $[\alpha]_{546}^{20} + 4.28^\circ$ (*c* 5.83, benzene). For $C_{22}H_{23}OP$ (334.4) calculated: 79.02% C, 6.93% H; found: 78.70% C, 6.63% H.

(2S,9S)-2,9-Dibenzyloxy-4,7-diphenyl-4,7-diphosphadecane (VIII). To a solution of 11 g (27 mmol) of 1,2-bis(diphenylphosphino)ethane in 150 ml of tetrahydrofuran, 3.5 g (0.5 mol) of lithium were added and the mixture was stirred at room temperature for 5 h. The red solution was

freed of the unreacted lithium by filtration through a glass wool and then 27 mmol of tert-butyl chloride were added to the filtrate under stirring. After 15 min reflux, the mixture was cooled to room temperature and 15.4 g (70 mmol) of tetrahydrofuran were added and the solution was stirred at ambient temperature for another 2 h. After the work-up, the resulting oil was purified by molecular distillation (bath temperature 170°C, $5 \cdot 10^{-6}$ Torr); $[\alpha]_{546}^{20} +3.73^\circ$ (*c* 3.5, benzene). For $C_{34}H_{40}O_2P_2$ (544.8) calculated: 74.95% C, 7.40% H; found: 74.52% C, 7.43% H.

(*S*)-2-Benzoyloxy-1,4-bis(diphenylphosphino)butane (IX). To a mixture of 62 g (0.33 mol) of diethyl ester of (*S*)-malic acid ($[\alpha]_D^{20} -10.29^\circ$ (*in substantia*), n_D^{20} 1.4323; reported¹⁹ $[\alpha]_D^{20} -10.11^\circ$ (*in substantia*), n_D^{20} 1.4362) and 171 g (1 mol) of benzyl bromide, 115 g (0.5 mol) of silver(I) oxide were added portionwise at ambient temperature under stirring which was continued for 30 min. After dilution with 200 ml of diethyl ether, the silver oxide was filtered-off, washed with the ether and the combined filtrates freed of the solvent. The residue was distilled and a fraction boiling at 138–143°C/3.5 Torr was collected. The crude product (106 g, $\alpha_{546}^{20} -42.46^\circ$ (*l* = 1, *in substantia*)) was dissolved in 200 ml of the ether and the solution was added dropwise to a suspension of 17 g (0.48 mol) of lithium aluminium hydride in 150 ml of the ether. The mixture was refluxed for 1 h and the excess hydride was decomposed.

The precipitate was filtered-off, extracted with the ether and the combined filtrate and extract were dried with magnesium sulphate. Distillation under reduced pressure afforded 31 g (50%) of (*S*)-2-benzoyloxy-1,4-butanediol boiling at 147–150°C/3 Torr; $[\alpha]_{546}^{20} -37.9^\circ$ (*c* 3.35, 96 v.% ethanol), n_D^{20} 1.5240. For $C_{11}H_{16}O_3$ (196.2) calculated: 67.32% C, 8.22% H; found: 67.12% C, 8.56% H.

A pyridine (50 ml) solution of 28 g (0.14 mol) of the diol described in the preceding paragraph was cooled to -10°C and 70.3 g (0.37 mol) of *p*-toluenesulphonyl chloride dissolved in 200 ml of pyridine were added in one portion. The solution was kept at 5°C for 19 h and poured onto ice (2 l). After standing for 30 min, the crushed cake was washed successively with 1.5 l of water and 60 ml of cold ethanol by which the initially bright red product decolorized. After drying on air, 44 g (63%) of the crude product were obtained. Its crystallization from ethanol yielded (*S*)-2-benzoyloxy-1,4-O-bis(4'-toluenesulphonyl)-1,4-butanediol; m.p. 93.0–93.5°C, $[\alpha]_{546}^{20} -34.5^\circ$ (*c* 3.14, chloroform). For $C_{25}H_{28}O_7S_2$ (504.2) calculated: 59.60% C, 5.99% H; found: 59.45% C, 5.68% H.

Phosphine IX was prepared similarly as phosphine X by the reaction of 15 g (29.7 mmol) of the tosylate described in the preceding paragraph with lithium diphenylphosphide prepared from 15 g (68 mmol) of chlorodiphenylphosphine and 2 g (0.29 mol) of lithium in tetrahydrofuran (150 ml). After stirring the mixture at room temperature for 2 h and the work-up, 11.2 g (71%) of a viscous liquid were obtained. The product IX was purified by chromatography on silica gel using acetone–hexane (1 : 4) as an eluent; $[\alpha]_{546}^{20} -29.4^\circ$ (*c* 4.7, benzene). For $C_{35}H_{34}OP_2$ (538.6) calculated: 78.95% C, 6.43% H; found: 78.62% C, 6.12% H.

(2*R*,3*R*)-2,3-O-Cyclohexylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (X). A solution of 75 g (0.26 mol) of diethyl ester of (2*R*,3*R*)-2,3-O-cyclohexylidene-tartaric acid ($[\alpha]_D^{20} -34.8^\circ$, *in substantia*), n_D^{20} 1.4568; reported²⁰ $[\alpha]_D^{20} -35.57^\circ$ (*in substantia*), n_D^{20} 1.4605) in 300 ml of the ether was added dropwise to a stirred suspension of 27 g (0.65 mol) of lithium aluminium hydride in 500 ml of the ether such that the mixture was kept under mild reflux. After completion of the addition, the mixture was refluxed for 3 h, the excess hydride was decomposed by 25 g of ethyl acetate, 27 g of water, 27 ml of 4*M*-NaOH and 80 ml of H₂O. The precipitate was filtered-off and extracted with ether. From the combined filtrate and extract dried over magnesium sulphate the ether was removed by distillation. Distillation of the residue gave 37 g (76%) of a fraction boiling at 134–136°C/1 Torr which readily crystallized. After recrystallization from diisopropyl

ether, the resulting 2,3-O-cyclohexylidene-L-threitol melted at 53–54°C; $[\alpha]_D^{20} - 5.56^\circ$ (*c* 3.56, chloroform). For $C_{10}H_{18}O_4$ (202.3) calculated: 59.39% C, 8.97% H; found: 59.51% C, 8.92%.

The product of the same purity was also obtained by the reduction of a mixture of ester-ketals that was obtained by the following procedure: A solution of 103 g (0.5 mol) of diethyl ester of (2*R*,3*R*)-tartaric acid, 108 g (0.75 mol) of 1,1-dimethoxycyclohexane and 300 mg of *p*-toluenesulphonic acid in 300 ml of benzene was kept under reflux while removing continuously a benzene-methanol azeotrope (b.p. 53°C) until the temperature of the vapours did not raise to 78°C. Then the mixture was cooled to room temperature and the catalyst was neutralized by potassium carbonate. After filtration and the removal of the solvent and 1,1-dimethoxycyclohexane, the residue was distilled to yield a fraction boiling at 149°C/1 Torr – 167°C/0.4 Torr (112 g) which according to chromatographic analysis consisted of three ester-ketals.

A solution of 75 g (0.39 mol) of *p*-toluenesulphonyl chloride in 200 ml of pyridine was added in one portion to a solution of 37 g (0.18 mol) of the 2,3-O-cyclohexylidene-L-threitol described in the preceding paragraph in 300 ml of pyridine cooled to –5°C. The mixture was allowed to stand at 5–7°C for 2 days and poured onto water with ice. The product was separated, washed with cold ethanol, dried on air (86.5 g, 80%) and recrystallized from ethanol to give (2*R*,3*R*)-2,3-O-cyclohexylidene-1,4-bis(4'-toluenesulphonyl)-L-threitol; m.p. 107.5–108°C, $[\alpha]_D^{20} - 13.82^\circ$ (*c* 6, chloroform). For $C_{24}H_{30}O_8S_2$ (510.2) calculated: 56.45% C, 5.92% H; found: 56.53% C, 5.89% H.

A solution of 20 g (0.04 mol) of the threitol in 60 ml of tetrahydrofuran was added during 30 min to lithium diphenylphosphide prepared from 22.1 g (0.1 mol) of chlorodiphenylphosphine and 2 g (0.28 mol) of lithium in 150 ml of the same solvent. After 1 h, the solvent was removed, the residue dissolved in 150 ml of water and the same volume of benzene and the mixture stirred for 30 min. The organic layer was separated, dried with magnesium sulphate, the benzene distilled-off, the solid dissolved in 100 ml of hot ethanol and the solution filtered while hot. The crystalline substance obtained after cooling the solution was purified by recrystallization from ethanol to give 17 g (80%) of the phosphine X; m.p. 118.5–120°C, $[\alpha]_D^{20} - 19.65^\circ$ (*c* 0.6, benzene). For $C_{34}H_{36}O_2P_2$ (538.6) calculated: 75.82% C, 6.74% H; found: 75.72% C, 6.70% H.

(2*R*,3*R*)-2,3-O-Cyclohexylidene-2,3-dihydroxy-1,4-bis(benzylphenylphosphino)butane (XI). A solution of 5.1 g (10 mmol) of (2*R*,3*R*)-2,3-O-cyclohexylidene-1,4-bis(4'-toluenesulphonyl)-L-threitol in 30 ml of tetrahydrofuran was added dropwise to lithium benzylphenylphosphide (prepared from 5 g (21 mmol) of benzyl(chloro)phenylphosphine and 0.7 g (0.1 mol) of lithium in 30 ml of tetrahydrofuran) under stirring which was continued for another 2 h. The work-up afforded 4.9 g (86%) of a liquid which was purified by thin-layer chromatography on silicagel (heptane-acetone (8 : 1) as an eluent); $[\alpha]_{546}^{20} - 17.5^\circ$ (*c* 2.22, benzene). For $C_{36}H_{40}O_2P_2$ (566.7) calculated: 76.30% C, 7.11% H; found: 75.95% C, 7.29% H.

(2*R*,3*R*)-2,3-O-Cyclohexylidene-2,3-dihydroxy-1,4-bis(cyclohexylphenylphosphino)butane (XII).

A solution of 36 g (70 mmol) of the tosylate of cyclohexylidene-L-threitol (*cf.* synthesis of X) in 100 ml of tetrahydrofuran was added dropwise to a solution of lithium cyclohexylphenylphosphide prepared from 54 g (200 mmol) of cyclohexyldiphenylphosphine and excess lithium in the same solvent. The mixture was worked-up similarly as in the case of phosphine X to yield 35 g (92%) of an oil which was purified by chromatography on silica gel, using hexane-acetone (4 : 1) as an eluent; $[\alpha]_{546}^{20} - 6.1^\circ$ (*c* 10, benzene). For $C_{34}H_{48}O_2P_2$ (550.7) calculated: 74.15% C, 8.79% H; found: 74.42% C, 8.50% H.

(2*R*,3*R*)-2,3-O-Cyclopentylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (XIII). 2,3-O-cyclopentylidene-1,4-bis(4'-toluenesulphonyl)-L-threitol was obtained by refluxing a benzene

solution of 10 g (23 mmol) of 1,4-bis(4'-toluenesulphonyl)-L-threitol $[\alpha]_{\text{D}}^{20} -4.1^\circ$ (*c* 2.06, acetone); reported²¹ $[\alpha]_{\text{D}}^{20} -4.6^\circ$ (*c* 2, acetone) and 30 ml (0.3 mol) of cyclopentanone in the presence of 80 mg of *p*-toluenesulphonic acid while removing the released water as a benzene-water azeotrope. The reaction was complete after 10 h. The mixture was treated with 2 g of potassium carbonate, the benzene removed by distillation under reduced pressure and the residue dissolved in 50 ml of hot ethanol. After cooling the solution to room temperature, 9.5 g (83%) of the crude product were obtained. Its recrystallization from ethanol gave the pure substance; m.p. 117–118°C, $[\alpha]_{\text{D}}^{20} -11.8^\circ$ (*c* 1.30, chloroform). For $\text{C}_{23}\text{H}_{28}\text{O}_8\text{S}_2$ (496.6) calculated: 55.63% C, 5.68% H; found: 55.59% C, 5.66% H.

The compound (7 g, 14.1 mmol) was reacted with lithium diphenylphosphide (prepared from 6.2 g (35 mmol) of chlorodiphenylphosphine and 0.7 g (100 mmol) of lithium) in tetrahydrofuran as described for phosphine *X* to give 4.6 g (62%) of the phosphine *XIII*, m.p. 90–91.5°C, $[\alpha]_{\text{D}}^{20} -19.9^\circ$ (*c* 0.5, benzene). For $\text{C}_{33}\text{H}_{34}\text{O}_2\text{P}_2$ (524.6) calculated: 75.56% C, 6.53% H; found: 75.56% C, 6.60% H.

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