SYNTHESIS OF AN OPTICALLY ACTIVE SILYLATED DIPHOSPHINE AND RELATED DINITRILE DERIVED FROM L-(+)-TARTARIC ACID*

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Synthesis of (3S,4S)-(+)-3,4-bis[3-(triethoxysilyl)propoxy]hexane-1,6-dinitrile and (2R,3R)-(−)--2-methyl-2-[4-(triethoxysilyl)butyl]-4,5-bis(diphenylphospinomethyl)-1,3-dioxolane is reported. The compounds are first examples of optically active alkoxysilanes containing diphenylphosphine and nitrile groups.

In the study of catalysts for asymmetric syntheses both heterogenous and homogeneous transition metal compounds have received attention in many laboratories. Kagan and coworkers[1-8] used a new chiral diphosphine, (−)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane (diop) in combination with rhodium to asymmetric hydrogenation and hydrosilylation. Rh-diop catalysts have been employed also by other authors[9-11]. The diphosphine was attached to an organic polymer which was used as the support of a heterogenized homogeneous rhodium catalyst[12]. Recently, inorganic supports have been modified with success by using bifunctional silanes which in addition to functional groups possessing coordinating ability toward transition metals contained alkoxy- or halogenosilyl substituents. The latter rendered it possible to chemically bond these compounds to the surface of the supports *via* interaction with surface hydroxy groups[13-15].

In the light of these results it seemed useful to prepare some chiral compounds of the latter type and to examine their applicability to asymmetric syntheses. These compounds should be derived from a readily accessible chiral substance, should contain nitrile or tertiary phosphine groups as potential ligands and also alkoxysilyl groups which would interact with an inorganic support. In the present work we report the synthesis of two substances of this type which were derived from L-(+)--tartaric acid as the starting compound. Their application to the modification of inorganic supports and to the synthesis of heterogenized transition metal catalysts will be the subject of a subsequent paper.

In the synthesis of the first compound, the dinitrile *VI*, diethyl ester of L-(+)--tartaric acid was reacted with allyl bromide to give diethyl (2R,3R)-(+)-2,3-diallyl-oxysuccinate(*I*) which was reduced by LiAlH₄ to (2S,3S)-(+)-2,3-diallyloxybutane--1,4-diol (*II*) The product was not, however, quite pure. Neither the reduction of

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diallyl $(2R,3R)$-$(+)$-2,3-diallyloxysuccinate (III) by $LiAlH_4$ yielded the pure diol II. The products contained a small amount of side products which could not be removed by distillation. The diol II was converted into the ditosylate IV which by treatment with NaCN gave the dinitrile V. This substance was reacted with triethoxysilane in the presence of a catalyst, yielding the pure dinitrile VI.
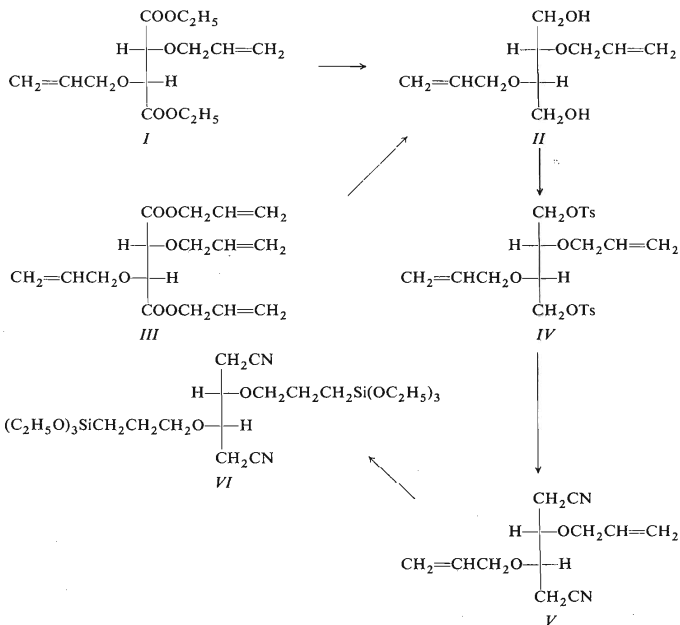
The second compound (Scheme 1) would be a substance derived from the acetal or ketal of optically active tartaric acid which is substituted with diphenylphosphine and trialkoxysilyl groups. Similar compounds have not yet been prepared.

We have tested first the reactions of diethyl L-$(+)$-tartrate with acrolein and methyl vinyl ketone using phosphorus pentoxide as a catalyst. However, polymerisation took place even in the presence of hydroquinone and the desired ketal or acetal was not obtained. Only the reaction of the diester with 3-butenyl methyl ketone produced the ketal, $(2R,3R)$-$(-)$-2-(3-butenyl)-2-methyl-4,5-diethoxycarbonyl-1,3-dioxolane
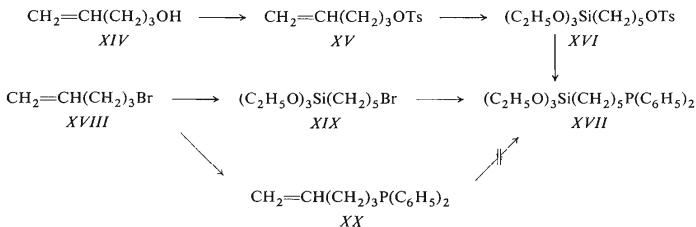
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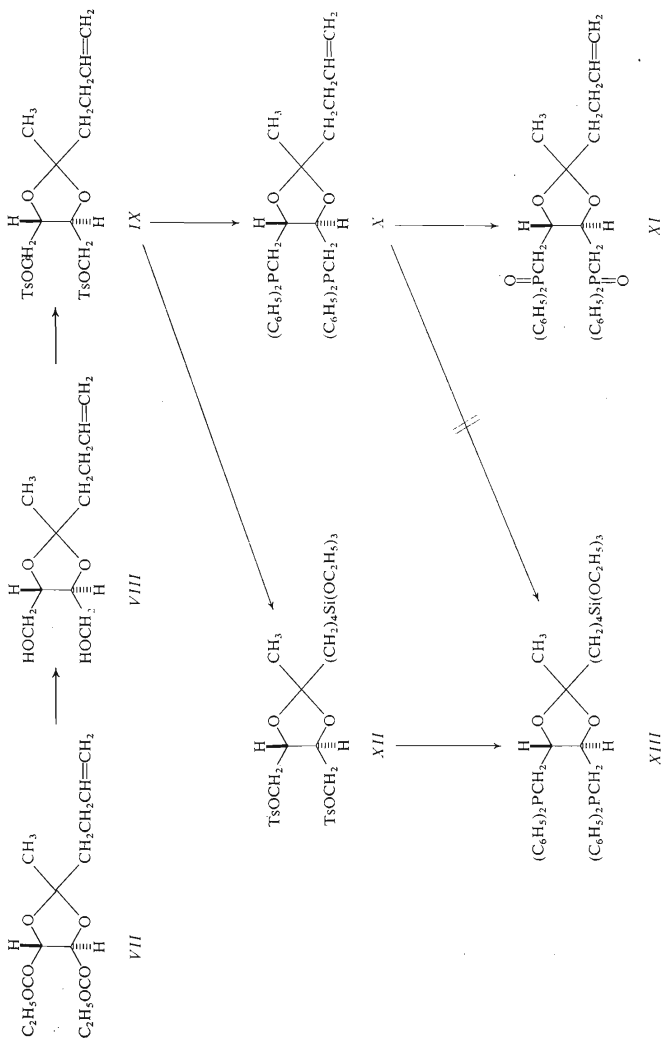
(*VII*). The reduction of this substance with lithium aluminium hydride gave the corresponding diol *VIII* which was converted into the crystalline ditosyl derivative *IX*. Treatment of the ditosylate with lithium diphenylphosphine yielded the pure, unsaturated diphospine *X*. Attempts at hydrosilylating the diphosphine *X* in the presence of $RhCl[P(C_6H_5)_3]_3$ have been unsuccessful. Under the conditions employed the reaction did not give the desired product *XIII*. This was confirmed both by the analysis of the isolated product and by its oxidation with hydrogen peroxide to the diphosphine oxide *XI*. This substance was obtained as a crystalline product both from the pure diphosphine *X* and from the reaction mixture, indicating that in the latter case the starting diphosphine *X* remained essentially unchanged under given reaction conditions.

Resulting from model experiments, $RhCl[P(C_6H_5)_3]_3$ was used as the catalyst for hydrosilylation of the ditosylate *IX* by triethoxysilane. As found by gel permeation chromatography, the isolated product *XII* contained several impurities. The serious problem connected with this procedure was the removal of the catalyst which had not to contaminate the resulting product. Since the crude product *XII* could not be purified by crystallization, the catalyst together with condensation products was removed by precipitation from a mixture of appropriate solvents. This method was found to yield the pure silylated derivative *XII*.

The diphosphine *XIII* was prepared from the silylated ditosylate *XII* by its reaction with $(C_6H_5)_2PLi$. Inverse procedure had to be used to suppress the reaction of the phosphide with the ethoxy group.

Substance *XIII*, which was obtained in sufficient purity, along with the dinitrile *VI*, exhibit the properties mentioned earlier.

$$CH_2{=}CH(CH_2)_3OH \longrightarrow CH_2{=}CH(CH_2)_3OTs \longrightarrow (C_2H_5O)_3Si(CH_2)_5OTs$$
$$XIV \qquad\qquad\qquad XV \qquad\qquad\qquad\qquad \downarrow XVI$$

$$CH_2{=}CH(CH_2)_3Br \longrightarrow (C_2H_5O)_3Si(CH_2)_5Br \longrightarrow (C_2H_5O)_3Si(CH_2)_5P(C_6H_5)_2$$
$$XVIII \qquad\qquad\qquad XIX \qquad\qquad\qquad\qquad XVII$$

$$CH_2{=}CH(CH_2)_3P(C_6H_5)_2$$
$$XX$$

In order to find an optimal procedure, individual steps of the synthesis have been tested with pentene-4-ol (*XIV*) as a model compound. The unsaturated alcohol *XIV* was converted into the tosylate *XV*, this in turn was hydrosilylated to form the product *XVI* which was then phosphinated to give substance *XVII*. This compound was obtained sufficiently pure. The same compound has been prepared also by another route,

via 4-pentenyl bromide *XVIII* and the silane *XIX*. Under reaction conditions used hydrosilylation of the unsaturated phosphine *XX* to compound *XVII* and the direct hydrosilylation of the alcohol *XIV* have not been successfull. In the latter case the reaction was accompanied by reesterification and formation of ethanol.

EXPERIMENTAL

Diethyl L-(+)-*tartrate* was prepared from L-(+)-tartaric acid by esterification with ethanol in the presence of hydrogen chloride[16]; b.p. 97—98°C/3 Torr, $[\alpha]_{546}^{20} +10.0°$ (ethanol, $c \pm 5.3$).

Diethyl (2R,3R)-(+)-2,3-*diallyloxysuccinate*(I). To a mixture of 800 ml of absolute ether and 9.6 g (0.4 mol) of sodium hydride pulver placed in a reaction flask dried by heating under nitrogen, 41.24 g (0.2 mol) of diethyl L-(+)-tartrate dissolved in 100 ml of ether were added dropwise during 45 min. After refluxing the mixture for one hour, the ether layer was separated from the solid portion and the solid was washed thrice with 500 ml of ether. Then, 200 ml of ether and 72.6 g (0.6 mol) of freshly distilled allyl bromide were added and the mixture was refluxed 3 h. The next day 20.4 g of allyl bromide were added and the reaction mixture was heated to the boiling point for 8 h. After dilution with ether to a total volume of 1500 ml, the solid portion was filtered off and the filtrate was freed from the solvent by distillation. A total of 27.6 g of the product was obtained which boiled at 96—98°C/0.3 Torr and contained the unreacted starting ester (10.3%) and two unidentified compounds (4.8% and 2.4%) (by g.l.c., 90 cm × 3 mm column filled with 1,4-butanediol succinate, hydrogen as a carrier gas). $[\alpha]_{546}^{20} +72.9°$ (ethanol, $c \pm 5.2$).

Diallyl (2R,3R)-(+)-2,3-*diallyloxysuccinate* (III). L-(+)-tartaric acid (60 g, 0.4 mol) was neutralized by 32 g of sodium hydroxide dissolved in water and the salt was treated with an aqueous solution of 135.9 g (0.8 mol) of silver nitrate to form the silver salt. This substance was filtered with suction, washed thoroughly with water and dried in the dark at 40°C and a pressure of 12 Torr, and then at 0.5 Torr. A total of 104.8 g of the product was obtained. Pulverized silver salt (154 g) was mixed with 300 g of silver(I) oxide (dried at 85°C/12 Torr, desintegrated and sifted through 0.315 mm-sieve) and 550 g of freshly distilled allyl bromide were added with stirring and shaking. After the initial exothermic reaction had subsided, the reaction mixture was heated 2 h on a boiling water bath. After cooling, the solid portion was filtered with suction and washed carefully with ether. Distillation yielded 85.9 g (65%) of the ester *III*, b.p. 115—117°C/0.5 Torr, For $C_{12}H_{22}O_6$ (310.4) calculated: 61.93% C, 7.15% H; found: 61.95% C, 7.14% H. $[\alpha]_{546}^{20} +92.6°$ (ethanol, $c \pm 5.3$). Its purity was verified by gas chromatography. Two studies[16,17] report the synthesis of methyl 2,3-dimethoxysuccinate by the reaction of silver tartrate with silver(I) oxide and methyl iodide.

(2S,3S)-(+)-2,3-*Diallyloxybutane*-1,4-*diol*(II). *a*) Preparation from the diethyl ester *I*. A solution of 7.16 g (25 mmol) of the ester in 50 ml of tetrahydrofurane was added with stirring to 2.15 g of LiAlH₄ dissolved in 150 ml of tetrahydrofurane. After the addion was complete (10 min), the mixture was refluxed for 10 min, cooled and decomposed successively with 2.1 ml of water, 2.1 ml of 15% NaOH and 6.3 ml of water. The precipitate was filtered off and washed. After solvent evaporation from the filtrate, distillation of the residue gave 2.92 g (57.7%) of the fraction which boiled at 99—102°C/0.3 Torr and contained 5% of the lower boiling impurity (by g.l.c.). For $C_{10}H_{18}O_4$ (202.3) calculated: 59.40% C, 8.97% H; found: 58.19% C, 8.95% H. $[\alpha]_{546}^{20} +2.3°$ (ethanol, $c \pm 5.5$).

b) Preparation from the diallyl ester *III*. A solution of the ester (90.2 g) in 500 ml of ether was added during 30 min to a solution of LiAlH₄ (22 g) in 600 ml of the same solvent. After 30 min-

-reflux, the mixture was cooled on ice bath and then slowly decomposed by 20% sulphuric acid until the mixture was neutral. The ether layer was separated and the aqueous layer was washed with 4 times 500 ml of ether. The extracts were combined, dried with sodium sulphate and the solvent was removed partially by evaporation. Distillation gave 45·2 g (77%) of the diol II of 87% purity; b.p. 107—108°C/0·5 Torr. $[\alpha]_{546}^{20}$ +5·1° (ethanol, $c \neq 5·4$). There are reports[2,16] on the reduction of methyl 2,3-dimethoxysuccinate with lithium aluminium hydride.

(3S,4S)-(+)-3,4-Diallyloxyhexane-1,6-dinitrile (V). The diol II (87% purity, 5·05 g) was dissolved in pyridine (32 g) and after cooling to −20°C 11·4 g of finely desintegrated *p*-toluenesulphonyl chloride were added. After standing overnight, the reaction mixture was poured onto ice and extracted with ether. The ether extracts were combined, washed successively with water, dilute hydrochloric acid, water and aqueous $NaHCO_3$. After drying with sodium sulphate, solvent removal by distillation and drying at 40°C and 0·5 Torr, 12·77 g of a lightly brown oil were obtained. The oil did not crystallize from common organic solvents. The ditosylate IV so prepared was dissolved in 74 g of dimethyl sulphoxide and finely divided sodium cyanide (4·1 g) was added to this solution. The reaction mixture, which spontaneously warmed up, was cooled to room temperature and set aside for one week. Then it was decomposed by water and extracted with dichloromethane. The combined extracts were washed with water, dried with magnesium sulphate and distilled to give 3·35 g of the dinitrile V boiling at 95—97°C/0·1 Torr. Its purity was verified by gas-liquid chromatography. For $C_{12}H_{16}O_2N$ (220·3) calculated: 65·43% C, 7·32% H, 12·72% N; found: 65·10% C, 7·32% H, 12·97% N. $[\alpha]_{546}^{20}$ +9·4° (ethanol, $c \neq 5·2$).

(3S,4S)-(+)-3,4-Bis[3-(triethoxysilyl)propoxy]hexane-1,6-dinitrile (VI). A mixture of 2·59 g of the dinitrile V, 6·0 g of triethoxysilane and 45 mg of Wilkinson catalyst, $RhCl[P(C_6H_5)_3]_3$, was heated to the boiling point for 4 h. The temperature of condensing vapours increased slowly from 138 to 155°C. After cooling, 1·88 g of a yellowish oil, b.p. 155—160°C/0·05 Torr, were obtained. For $C_{24}H_{48}N_2O_8Si_2$ (548·8) calculated: 52·52% C, 8·82% H, 10·24% Si; found: 52·39% C, 8·71% H, 10·28% Si. $[\alpha]_{546}^{20}$ +6·7° (l = 1, *in substantia*).

The reaction of diethyl L-(+)-tartrate with acrolein and with methyl vinyl ketone. The diethyl ester and the same weight amount of acrolein or methyl vinyl ketone were mixed and then phosphorus pentoxide was slowly introduced into this mixture with stirring and external cooling with water. The black slurry formed was cooled and extracted with ether. Except for the unreacted diethyl ester, other pure products have not been isolated. Condensation and polymerisation reactions took place even in the presence of hydroquinone.

(2R,3R)-(−)-2-(3-Butenyl)-2-methyl-4,5-diethoxycarbonyl-1,3-dioxolane (VII). To a mixture of 55·8 g (0·27 mol) of diethyl L-(+)-tartrate and 49·5 g of 3-butenyl methyl ketone (obtained from allyl chloride and sodium ethyl acetoacetate), 150 ml of benzene and 0·25 g of *p*-toluenesulphonic acid were added and the mixture was heated to the boiling point for 42 h while removing continuously the reaction water by azeotropic distillation. After standing 3 days, the reaction mixture was washed with saturated aqueous borax solution and dried by magnesium sulphate. Distillation yielded a fraction boiling at 83—95°C/0·2 Torr (28·05 g), $[\alpha]_{546}^{20}$ −20·45° (ethanol, $c \neq 5·2$) and another fraction boiling at 95—98°C/0·2 Torr (24·07 g), $[\alpha]_{546}^{20}$ −28·4° (ethanol, $c \neq 5·1$). As found by gas chromatographic analysis, the former fraction contained a small amount of impurities, while the latter fraction was chromatographically pure. For $C_{14}H_{22}O_6$ (286·3) calculated: 58·73% C, 7·74% H; found: 58·93% C, 7·76% H.

(2S,3S)-(+)-2-(3-Butenyl)-2-methyl-4,5-bis(hydroxymethyl)-1,3-dioxolane (VIII). A solution of 22·63 g (79 mmol) of the diester VII in 100 ml of ether was added slowly with stirring to a solution of 6·0 g (158 mmol) of LiAlH₄ in 150 ml of ether. After refluxing the reaction mixture for 2 h, the mixture was diluted with 200 ml of ether and decomposed by adding successively 6 ml of water,

6 ml of 16% NaOH and 18 ml of water. The precipitated aluminium salts were repeatedly extracted with warm ether, the ether extracts were combined, dried by magnesium sulphate and the solvent was partially removed by evaporation. Distillation of the residual liquid gave 12·98 g of the product, b.p. 98—100°C/0·2 Torr, $[\alpha]_{546}^{20}$ +3·6° (ethanol, $c \doteq 5·1$). For $C_{10}H_{18}O_4$ (202·3) calculated: 59·39% C, 8·97% H; found: 59·80% C, 9·09% H. Its purity was confirmed by gas–liquid chromatography. There are reports[2,18-20] on the reduction of 2,2-dimethyl-4,5-diethoxycarbonyl-1,3-dioxolane to the corresponding diol using $LiAlH_4$ as the reducing agent.

(2S,3S)-(−)-2-(3-Butenyl)-2-methyl-4,5-bis(hydroxymethyl-p-toluenesulphonate)-1,3-dioxolane (IX). A solution of 24·9 g (0·123 mol) of the diol *VIII* in 227 g of pyridine was cooled to −20°C and then 49·8 g (0·262 mol) of p-toluenesulphonyl chloride powder were added during 10 min. The reaction mixture was allowed to stand overnight at 0°C, decomposed by water and extracted with benzene. The extracts were combined, washed with water and dried with magnesium sulphate. After partial solvent removal by evaporation under reduced pressure at a maximal bath temperature of 45°C, the residual oil was crystallized from ethanol to yield 48·8 g of a crystalline product which after recrystallization afforded the pure product (46·5 g), m.p. 67—68°C. For $C_{24}H_{30}S_2O_8$ (510·6) calculated: 56·45% C, 5·92% H; found: 56·44% C, 5·88% H. $[\alpha]_{546}^{20}$ −16·3° (ethanol, $c \doteq 3·1$). ¹H-NMR spectrum (δ scale): 7·45 (quadruplet, aromatic protons), 5·95—4·66 (multiplet, vinylic protons), 1·15 (CH_3 protons on the quarternary carbon), 2·37 (protons of the methyl on the aromatic ring), 1·63 and 3·95 (protons of CH_2 and CH groups, mutually unresolved). Integration confirmed the suggested structure.

(2R,3R)-(−)-2-(3-Butenyl)-2-methyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane (X). To a solution of $(C_6H_5)_2PLi$ (prepared from 10·5 g (66·6 mmol) of bromobenzene, 12·4 g (66·6 mmol) of diphenylphosphine and lithium in 50 ml of ether), a solution of the ditosylate *IX* in benzene was slowly added under nitrogen with stirring so long as the reaction mixture remained orange. A total of 13·3 g (26·1 mmol) of the ditosylate was added. The reaction mixture was heated to the boiling point for 1 h, decomposed with water (deoxygenated by boiling and cooled under nitrogen). The benzene extracts were dried by magnesium sulphate and the solvent was partially evaporated at reduced pressure. The unreacted diphenylphosphine was removed by heating to 150°C at a pressure of 0·05 Torr for 2 h. The product was a yellowish, very viscous oil. For $C_{34}H_{36}O_2P_2$ (538·6) calculated: 75·82% C, 6·74% H; found: 76·19% C, 7·37% H.

Attempted hydrosilylation of diphosphine X. A mixture of 11·1 g of the diphosphine *X* and 10·4 g of triethoxysilane was heated to the boling point in the presence of 47 mg of $RhCl[P(C_6H_5)_3]_3$ for 7 h. After standing for one week, the solution was filtered through a sintered glass filter to remove a small amount of an insoluble portion and then the solvent was evaporated at 100°C and 0·05 Torr, which took 4 h. By this procedure 11·82 g of a brown oil was obtained which did not yield satisfactory analysis. The oil was dissolved in acetone and oxidized by 30% hydrogen peroxide with external cooling by ice water until the reaction on the iodine-starch paper was positive. The reaction mixture was then diluted with the same volume of water, made alkaline by aqueous NaOH solution and extracted with benzene. The combined extracts were dried by magnesium sulphate, the solvent evaporated and the residue recrystallized from benzene. The product obtained (4·93 g) was once more recrystallized from benzene to give the compound melting at 181°C. No mixed melting point depression has been observed for the mixture of this product with the substance *XI* which was obtained by the oxidation of the diphosphine *X* by hydrogen peroxide carried out in the above-mentioned way. For $C_{34}H_{36}O_4P_2$ (570·6) calculated: 71·57% C, 6·36% H; found: 70·84% C, 6·28% H.

(2S,3S)-(−)-2-Methyl-2-[4-(triethoxysilyl)butyl]-4,5-bis-(hydroxymethyl-p-toluenesulphonate)-1,3-dioxolane (XII). A mixture of 20·45 g of the ditosylate *IX*, 25·4 g of triethoxysilane and 254 mg

of RhCl[P(C_6H_5)$_3$]$_3$ was heated under nitrogen to the boiling point for 7·5 h. After evaporation at 100°C and 0·1 Torr, 27·3 g of a dark brown oily product were obtained. The product was dissolved in 250 ml of ether and diluted with 250 ml of ether. After standing overnight, the solution was separated from the solid portion (total amount 5·2 g) containing the catalyst and filtered after addition of active charcoal. After evaporation of volatile compounds at 100°C/0·2 Torr, 14·7 g of a brown oil were obtained. For $C_{30}H_{46}O_{11}S_2Si$ (674·9) calculated: 53·35% C, 6·87% H; found: 52·69% C, 6·67% H. $[\alpha]_{546}^{20}$ −11·5° (benzene, $c = 11$). ^{1}H-NMR spectrum (δ scale): 7·45 (quadruplet, aromatic protons), 2·37 (CH_3 protons on the aromatic ring), 1·31 (CH_3 protons on the quarternary carbon), 1·11 (centre of the triplet of CH_3 protons of the ethoxy group, coupling constant 7 Hz), 3·66 (centre of the quadruplet of CH_2 protons of the ethoxy group, coupling constant 7 Hz), 3·95 (CH_2 and CH protons, mutually unresolved), 5·95−4·66 (a weak multiplet of vinylic protons). The spectrum confirmed the presence of a small amount of the starting compound.

(2R,3R)-(−)-2-Methyl-2-[4-(triethoxysilyl)butyl]-4,5-bis-(diphenylphosphinomethyl)-1,3-dioxolane (XIII). To a solution of (C_6H_5)$_2$PLi (obtained from 8·55 g (55 mmol) of bromobenzene, excess lithium and 10·2 g (55 mmol) of diphenylphosphine in 150 ml of ether), 14·7 g (22 mmol) of the ethoxysilylated ditosylate *XII* dissolved in 150 ml of benzene were added during 30 min with stirring. After 1 h-standing, the mixture was decomposed by the water deoxygenated by boiling and cooled under nitrogen. The benzene–ether layer was separated, dried by potassium carbonate and the solvent evaporated at 95°C and 1 Torr. All manipulations were carried out in an atmosphere of nitrogen. A total of 16·3 g of a brown, very viscous oil was obtained; $[\alpha]_{546}^{20}$ −15·1° (benzene, $c \neq 7$). For $C_{40}H_{52}O_5P_2Si$ (702·9) calculated: 68·35% C, 7·46% H; found: 68·95% C, 6·96% H. ^{1}H-NMR spectrum (δ scale): 7·13 (singlet with a wide base, aromatic protons), 3·66 (centre of the quadruplet of CH_2 protons of the ethoxy group), 1·11 (centre of the triplet of CH_3 protons of the ethoxy group), 1·15 (CH_3 protons on the quarternary carbon), 2·22 and 1·15 (centres of doublet and multiplet for CH_2 and CH protons which could not be resolved and which overlapped with the CH_3 protons on the quarternary carbon and with CH_3 protons of the ethoxy group).

Pentene-4-ol-p-toluenesulphonate (XV). To a solution of 8·6 g (0·1 mol) of pentene-4-ol (b.p. 136−138°C) in 120 ml of dry pyridine cooled to −15°C, 20 g of finely desintegrated *p*-toluenesulphonyl chloride were added during 2 min, and the mixture was allowed to stand overnight at +5°C. The reaction mixture was decomposed by pouring onto ice and extracted by ether. The ether extracts were dried by magnesium sulphate and the undissolved crystalline residue (*p*-toluenesulphonic acid) was filtered off. Distillation of the extract gave 14·09 g (58·5%) of the product boiling at 108−110°C/0·2 Torr. The sample decomposed during gas chromatographic analysis. For $C_{12}H_{16}O_3S$ (240·3) calculated: 59·97% C, 6·71% H; found: 60·04% C, 6·57% H.

5-(Triethoxysilyl)pentanol-p-toluenesulphonate (XVI). A mixture of 13·56 g of the tosylate *XV*, 15 g of triethoxysilane and 70·6 mg of RhCl[P(C_6H_5)$_3$]$_3$ was refluxed 6 h. After distilling-off the silane at reduced pressure, 6·65 g of the product were obtained by vacuum distillation; b.p. 165−170°C/0·2 Torr. The product contained a small amount of impurities.

Triethoxy(5-bromopentyl)silane (XIX). A mixture of 14·9 g (0·1 mol) of 4-pentenyl bromide, 18 g (0·11 mol) of triethoxysilane and 76 mg of RhCl[P(C_6H_5)$_3$]$_3$ was refluxed under nitrogen for 2·5 h. The progress of hydrosilylation reaction was followed by gas chromatography. Distillation yielded 23·6 g of the silane *XIX*, b.p. 140−141°C/12 Torr. For $C_{11}H_{25}O_3BrSi$ (313·3) calculated: 42·17% C, 8·04% H; found: 42·14% C, 7·98% H. On using hexachloroplatinic acid as the catalyst (0·1 N solution in isopropanol − 3 drops), the silylated product was formed at a much slower rate than in the presence of Wilkinson catalyst.

Triethoxy(5-diphenylphosphinopentyl)silane (XVII). *a*) To a solution of $(C_6H_5)_2PLi$ (prepared from 7·9 g of triphenylphosphine, excess lithium and 2·81 g of tert-butyl chloride in tetrahydrofurane), 9·4 g of the silane *XIX* dissolved in tetrahydrofurane were added during 30 min. After solvent removal by distillation under normal and reduced pressures, benzene was added to the residue and inorganic salts were filtered-off and washed. Distillation of the filtrate gave 6·45 g of the silane *XVII* boiling at 178—180°C/0·1 Torr. For $C_{23}H_{35}O_3PSi$ (418·4) calculated: 66·03% C, 8·43% H, 6·71% Si; found: 66·20% C, 8·30% H, 6·54% Si. *b*) A solution of $(C_6H_5)_2PLi$ prepared from 4·45 g of triphenylphosphine, excess lithium and 1·60 g of tert-butyl chloride was added to 6·65 g of the tosylate *XVI* dissolved in tetrahydrofurane. The addition was complete after 1 h. Then the reaction mixture was refluxed 3 h, cooled, the inorganic salts filtered-off and washed. Distillation of the filtrate yielded 2·22 g of the silane *XVII*, b.p. 180—183°C/0·1 Torr, which contained a small amount of impurities (by g.l.c.).

4-Pentenyldiphenylphosphine (XX). A solution of $(C_6H_5)_2PLi$ prepared from 15·74 g of triphenylphospine, 5·61 g of tert-butyl chloride and excess lithium in tetrahydrofurane was divided into two halves. The first one was introduced into a solution of 4·5 g of 4-pentenyl bromide in 21 g of tetrahydrofurane. The solution of the phosphine immediately decolourized. The reaction mixture was refluxed 1 h, and the solvent was evaporated under reduced pressure. Distillation gave 6·4 g (84%) of the phosphine *XX*, b.p. 138—143°C/1·9 Torr. The other half was placed into a reaction flask to which a solution of 4·5 g of 4-pentenyl bromide in tetrahydrofurane (total volume 25 ml) was slowly introduced. After 19 ml of the solution had been added, the phosphine solution turned colourless and the addition was stopped. The reaction mixture was heated to the boiling point for 1 h and then the solvent was removed by evaporation. Distillation yielded 5·38 g (70·6%) of the phosphine, b.p. 126—128°C/0·7—0·8 Torr. Both fractions were combined and distilled to give the product boiling at 115—116°C/0·25 Torr. Its purity was verified by gas chromatography.

Reaction of 4-pentenyldiphenylphosphine (XX) *with triethoxysilane*. A mixture of 8·92 g of the phosphine, 5·77 g of triethoxysilane and 84 mg of $RhCl[P(C_6H_5)_3]_3$ was heated to the boiling point for 4 h. Distillation gave a fraction boiling at 166—175°C/0·1 Torr which was analysed by gas chromatography. The analysis showed that the fraction contains a number of compounds which could not be separated by distillation.

Reaction of pentene-4-ol (XIV) *with triethoxysilane*. The treatment of equivalent amounts of both components in the presence of Wilkinson catalyst was found to lead to reesterification by which ethanol is formed, along with other unidentified products.

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