

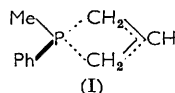
The Rearrangement of Allylic Phosphines

By M. P. Savage and S. Trippett, Department of Chemistry, The University, Leicester

Reduction of the allylic phosphine oxides, $\text{Ph}_2\text{P}(\text{O})\text{CR}^1\text{R}^2\text{-CH:CH}_2$, with phenylsilane followed by rapid distillation gives the crude allylic phosphines, $\text{Ph}_2\text{P-CR}^1\text{R}^2\text{-CH:CH}_2$, which rearrange at 210° to the more stable phosphines $\text{Ph}_2\text{P-CH}_2\text{CH:CR}^1\text{R}^2$. This rearrangement is catalysed by traces of silanes or silanols; the pure allylic phosphines do not rearrange under these conditions. Diphenyl-(1-phenylallyl)phosphine gave with methyl iodide the prototropically rearranged methylidiphenyl-(1-phenylprop-1-enyl)phosphonium iodide.

HORNER and his co-workers¹ showed that optically active allylmethylphenylphosphine racemised readily on refluxing in toluene solution and suggested that this occurred by allylic rearrangement, presumably *via* a symmetrical transition state (I). Our recent synthesis of allylic diphenylphosphine oxides² gave us the opportunity of investigating this proposed allylic rearrangement.

Reduction of diphenyl-(1-phenylallyl)phosphine oxide (II; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$) with lithium aluminium hydride gave a mixture of products containing diphenylphosphines as well as the expected phosphine. The reduction



(I)



(II)

was therefore carried out with phenylsilane³ at 140° and the diphenyl-(1-phenylallyl)phosphine obtained by a rapid distillation at $\sim 190^\circ/0.6$ mm. The structure followed from the absorption in the i.r. at 985 and 920 cm^{-1} , characteristic of a vinyl group, coupled with the absence of absorption at 1180 cm^{-1} , characteristic of phosphine oxides. The phosphine on oxidation gave the original oxide but with methyl iodide the rearranged

methiodide $\text{MePh}_2\text{P}^+\text{-CPh:CHMe I}^-$ was formed. The crude distilled phosphine remained unchanged on keeping at 120° for 16 hr. but at 210° rearranged smoothly to cinnamylidiphenylphosphine, $\text{Ph}_2\text{PCH}_2\text{CH:CHPh}$. This with benzaldehyde and acrylonitrile in refluxing ethanol⁴ gave 1,4-diphenylbuta-1,3-diene.

Similar sequences of reduction, rapid distillation to give crude unrearranged allylic phosphine, and rearrangement at 210° to a more stable allylic phosphine were carried out starting with a number of allylic phosphine oxides of the general formula $\text{Ph}_2\text{P}(\text{O})\text{CR}^1\text{R}^2\text{-CH:CH}_2$ (see Experimental section). Of these, linalyldiphenylphosphine oxide was prepared by the rearrangement of geranyl diphenylphosphinite, which also gave some geranyldiphenylphosphine oxide. However, when diphenyl-(1-phenylallyl)phosphine was subsequently obtained crystalline, the pure compound did not rearrange at 210° . Indeed, all attempts to catalyse rearrangement of the pure phosphine by the addition of acid or base at this temperature failed, but the rearrangement could be brought about by the addition of phenylsilane. Presumably the rapidly-distilled crude allylic phosphines contained sufficient silane or silanol to catalyse the subsequent rearrangements.

¹ L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Letters*, 1961, 161.

² M. P. Savage and S. Trippett, *J. Chem. Soc. (C)*, 1966, 1842.

³ H. Fritzsche, V. Hasserodt, and F. Korte, *Chem. Ber.*, 1964, 97, 1988.

⁴ S. Trippett, *Chem. Comm.*, 1966, 468.

EXPERIMENTAL

All reactions were carried out under oxygen-free nitrogen. Light petroleum had b. p. 60–80°. N.m.r. spectra were recorded in deuteriochloroform with tetramethylsilane as internal standard on a Varian Associates A60 spectrometer. Oxidation of phosphines to phosphine oxides was carried out by shaking a benzene solution of the phosphine with hydrogen peroxide (100 vol.) at room temperature.

Rearrangement of Crude Diphenyl(1-phenylallyl)phosphine.—A mixture of diphenyl(1-phenylallyl)phosphine oxide (4.25 g.) and phenylsilane (3 g.) was kept at 140° for 2 hr. and distilled rapidly to give crude diphenyl(1-phenylallyl)phosphine (3.3 g.), b. p. 190–195°/0.6 mm. Oxidation of an aliquot gave the original oxide, m. p. and mixed m. p. 193–193.5°. Treatment of a benzene solution with methyl iodide gave *methyldiphenyl(1-phenylprop-1-enyl)-phosphonium iodide*, m. p. 172–173° (from chloroform-ethyl acetate), doublet (3H) at τ 7.26 ($J_{PH} = 13$ c./sec.), quartet (3H) at τ 8.06 ($J_{PH} = 3$, $J_{HH} = 7$ c./sec.) (Found: C, 59.4; H, 4.9; P, 7.1. $C_{22}H_{22}IP$ requires C, 59.6; H, 5.0; P, 7.0%). The i.r. spectrum contained no evidence of a vinyl group.

The above crude phosphine was kept at 210° for 5 hr. to give cinnamylidiphenylphosphine, ν_{max} 960 cm^{-1} . Oxidation of an aliquot gave cinnamylidiphenylphosphine oxide, m. p. and mixed m. p. 181–182° (from benzene–light petroleum), having an i.r. spectrum identical with that of an authentic sample. Treatment in benzene with methyl iodide gave *cinnamylmethyldiphenylphosphonium iodide*, m. p. 156–157° (from chloroform–ethyl acetate), ν_{max} 970 cm^{-1} , quartet (2H) at τ 5.64 ($J_{PH} = 16$, $J_{HH} = 8$ c./sec.) complex (1H) centred on τ 4.0 (Found: C, 59.4; H, 4.9; P, 7.15. $C_{22}H_{22}IP$ requires C, 59.6; H, 5.0; P, 7.0%).

A solution of the above cinnamylidiphenylphosphine (1.4 g), benzaldehyde (0.5 g.), and acrylonitrile (0.6 g.) in ethanol (30 ml.) was refluxed for 15 hr. and the solvent removed under reduced pressure. Chromatography of the residue on basic alumina (10 g.) gave 1,4-diphenylbuta-1,3-diene (0.4 g.), m. p. and mixed m. p. 154–155°.

Rearrangement of Pure Diphenyl(1-phenylallyl)phosphine.—A mixture of diphenyl(1-phenylallyl)phosphine oxide (6 g.) and phenylsilane (4 g.) was kept at 150° for 4 hr. and the excess of silane then removed under reduced pressure. Aqueous sodium hydroxide (40 ml., 20%) was then added and the suspension heated under reflux for 1/2 hr., cooled, and extracted with benzene (2 \times 50 ml.). The extract was washed with water, dried, and evaporated. Crystallisation of the residue from aqueous methanol gave diphenyl(1-phenylallyl)phosphine (2.3 g.), m. p. 74–76°, ν_{max} 1630, 985, and 920 cm^{-1} . Oxidation gave the oxide, m. p. and mixed m. p. 193–194°, and treatment with methyl iodide gave *methyldiphenyl(1-phenylprop-1-enyl)-phosphonium iodide*, m. p. and mixed m. p. 172–173°. The phosphine was unchanged on keeping at 220° for 15 hr.

A mixture of diphenyl(1-phenylallyl)phosphine (0.4 g.) and phenylsilane (0.06 g.) was kept at 220° for 2 hr. when absorption at 985 and 920 cm^{-1} ($CH:CH_2$) had been largely replaced by absorption at 965 cm^{-1} (*trans*- $CH:CH$). The mixture was boiled with aqueous sodium hydroxide (5 ml., 20%) for 1/2 hr., cooled, and extracted with benzene. The

extract was dried and evaporated. Oxidation of the residue gave cinnamylidiphenylphosphine oxide (0.25 g.), m. p. and mixed m. p. 181–182°.

Linalyldiphenylphosphine Oxide.—Chlorodiphenylphosphine (11 g.) in ether (10 ml.) was added slowly to geraniol (7.7 g.) and pyridine (9 ml.) in ether (50 ml.) cooled in ice. The suspension was filtered and the filtrate evaporated. The residue was then kept at 160° for 1/2 hr. and chromatographed on basic alumina (60 g.). Elution with benzene gave an oil which on trituration with light petroleum gave geranyldiphenylphosphine oxide (1.25 g.), m. p. and mixed m. p. 113–114°. Evaporation of the mother-liquor gave *linalyldiphenylphosphine oxide* (6.4 g.), m. p. 68–69° (from light petroleum), ν_{max} 1170, 995, and 910 cm^{-1} (Found: C, 78.1; H, 7.9; P, 9.3. $C_{22}H_{27}OP$ requires C, 78.2; H, 8.0; P, 9.2%).

A mixture of the above oxide (3.5 g.) and phenylsilane (2 g.) was kept at 140° for 3 hr. and distilled to give crude linalyldiphenylphosphine (2.6 g.), b. p. 180–200°/0.4 mm. The phosphine was kept at 200° for 3 hr. and oxidised to give geranyldiphenylphosphine oxide, m. p. and mixed m. p. 113–114° (from benzene–light petroleum).

1,1-Dimethylallyldiphenylphosphine Oxide.—Chlorodiphenylphosphine (10.8 g.) in ether (20 ml.) was added slowly to 3-methylbut-2-en-1-ol (4.2 g.) and pyridine (9 ml.) in ether (50 ml.) cooled in ice. The suspension was filtered and the filtrate evaporated and the residue kept at 140° for 1/2 hr. Crystallisation from benzene–light petroleum gave 1,1-dimethylallyldiphenylphosphine oxide (7 g.), m. p. 105–106°, ν_{max} 1180, 990, and 917 cm^{-1} , doublet (6H) at τ 8.7 ($J_{PH} = 14$ c./sec.) (Found: C, 75.7; H, 7.2; P, 11.7. $C_{17}H_{19}OP$ requires C, 75.6; H, 7.0; P, 11.5%).

Rearrangement of 1,1-Dimethylallyldiphenylphosphine.—A mixture of 1,1-dimethylallyldiphenylphosphine oxide (4 g.) and phenylsilane (3 g.) was kept at 140° for 4 hr. and rapidly distilled to give crude 1,1-dimethylallyldiphenylphosphine (3.2 g.), b. p. 160–165°/1 mm. Treatment with methyl iodide in benzene gave (1,1-dimethylallyl)methyl-diphenylphosphonium iodide, m. p. 119–120° (from chloroform–ethyl acetate), ν_{max} 990 and 925 cm^{-1} (Found: C, 54.8; H, 5.4; P, 8.0. $C_{18}H_{22}IP$ requires C, 54.6; H, 5.55; P, 7.8%). The phosphine was kept at 200° for 3 hr. and oxidised to give 3-methylbut-2-enyldiphenylphosphine oxide, m. p. and mixed m. p. 124–150° (from light petroleum).

Rearrangement of 1-Methylallyldiphenylphosphine.—A mixture of 1-methylallyldiphenylphosphine oxide (4.2 g.) and phenylsilane (3 g.) was kept at 120° for 3 hr. and rapidly distilled to give 1-methylallyldiphenylphosphine (3.6 g.), ν_{max} 990 and 910 cm^{-1} ($CH:CH_2$) with no absorption at 1180 cm^{-1} ($P:O$). Oxidation of an aliquot gave the original oxide, m. p. and mixed m. p. 90–91°. The phosphine was kept at 200° for 4 hr. when absorption due to vinyl had been replaced by strong absorption at 960 cm^{-1} (*trans*- $CH:CH$). Oxidation then gave but-2-enyldiphenylphosphine oxide, m. p. and mixed m. p. 115–116° (from benzene–light petroleum).

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