548. *The Rearrangement of* 1-*Hydroxyalkylphosphines to Alkylphosphine Oxides.*

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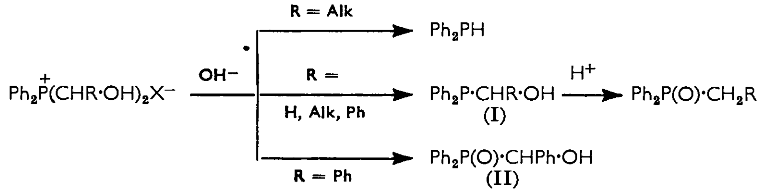
Di-(1-hydroxyalkyl)diphenylphosphonium halides, treated with aqueous alkali to pH 9, give 1-hydroxyalkyldiphenylphosphines. The corresponding phosphine oxide and diphenylphosphine may also be formed. The 1-hydroxyalkylphosphines, with toluene-*p*-sulphonic acid, in refluxing acetic acid, rearrange to alkylphosphine oxides, but hydroxymethyldiphenylphosphine, with toluene-*p*-sulphonic acid, in refluxing toluene, gives diphenylphosphine. This reaction was applied to the conversion of phenylphosphine into methylphenylphosphine.

IN an attempt to prepare bromomethyldiphenylphosphine, methoxymethyldiphenylphosphine (obtained by the reduction of the phosphine oxide with lithium aluminium hydride) was refluxed in acetic acid while dry oxygen-free hydrogen bromide was passed through the solution for 8 hr. The major product was methyldiphenylphosphine oxide. This was probably formed *via* the ion $Ph_2P{\cdot}\overset{+}{C}H_2 \longleftrightarrow Ph_2\overset{+}{P}{:}CH_2$; such ions would be formed from 1-hydroxyalkyldiphenylphosphines on suitable acid-treatment, and similar rearrangements were therefore sought among these compounds.

The 1-hydroxyalkyldiphenylphosphines, $Ph_2P{\cdot}CHR{\cdot}OH$ (R = H, Et, Pr^n, or Ph), all rearranged when refluxed in acetic acid with toluene-*p*-sulphonic acid, giving the alkylphosphine oxides, $Ph_2P(O){\cdot}CH_2R$. The hydroxymethylphosphine (I; R = H) also gave some 48% of the acetate, $Ph_2P{\cdot}CH_2{\cdot}OAc$, which was isolated as the methiodide. The high yield of acetate after a long reaction time indicates that it is not an intermediate in formation of the phosphine oxide.

The 1-hydroxyalkylphosphines were obtained by the action of aqueous alkali on di-(1-hydroxyalkyl)diphenylphosphonium halides, $[Ph_2P(CHR{\cdot}OH)_2]^+X^-$, themselves prepared from diphenylphosphine and an aldehyde under appropriate acidic conditions. Hydroxymethyl- and α-hydroxybenzyl-diphenylphosphine obtained in this way were free from diphenylphosphine, as shown by the absence of P–H absorption in the infrared spectrum at ~4·35 μ, but 1-hydroxyalkyl substituents proved to be very sensitive to alkali, and the crude 1-hydroxyalkylphosphines $Ph_2P{\cdot}CHR{\cdot}OH$ where R = Et or Pr^n contained about 70% of diphenylphosphine. The action of aqueous alkali on the di-(α-hydroxybenzyl)phosphonium salt also gave α-hydroxybenzyldiphenylphosphine oxide (II).



Buckler[1] has shown that the product from the reaction of phosphine, benzaldehyde, and hydrogen chloride in ether is benzyldi-(α-hydroxybenzyl)phosphine oxide, and suggested a secondary phosphine oxide, $Ph{\cdot}CH(OH){\cdot}PH(O){\cdot}CH_2Ph$, as an intermediate. Such an oxide could be formed by a rearrangement of di-(α-hydroxybenzyl)phosphine analogous to those described above; the observed product could also be formed by a similar rearrangement of tri-(α-hydroxybenzyl)phosphine.

When hydroxymethyldiphenylphosphine was refluxed in toluene with toluene-*p*-sulphonic acid, no phosphine oxide was formed. Instead paraformaldehyde accumulated

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[1] Buckler, *J. Amer. Chem. Soc.*, 1960, **82**, 4215.

in the condenser and diphenylphosphine (78%) was isolated. This ready removal of a hydroxymethyl group was used in the conversion of phenylphosphine into methylphenylphosphine. Phenylphosphine with formaldehyde and hydrochloric acid gave a solution containing tri(hydroxymethyl)phenylphosphonium chloride.[2] This solution, when made alkaline, gave di(hydroxymethyl)phenylphosphine, which on quaternisation with methyl iodide and treatment with alkali gave crude (hydroxymethyl)-methylphenylphosphine. Removal of the hydroxymethyl group gave methylphenylphosphine. The overall yield from phenylphosphine was low (15%). The secondary phosphine was characterised by reaction with benzyl bromide to give benzylmethylphenylphosphonium bromide. With aqueous alkali this gave benzylmethylphenylphosphine, identified as the methiodide. Similarly diphenylphosphine with benzyl bromide gave benzyldiphenylphosphonium bromide which with alkali gave the stable, crystalline, benzyldiphenylphosphine.

From the action of hydrogen bromide in acetic acid on methoxymethyldiphenylphosphine, the minor product, after treatment with methyl iodide, was dimethyldiphenylphosphonium iodide. Similarly the quaternary iodides obtained on rearrangement of the crude 1-hydroxyalkyldiphenylphosphines and treatment of the products with methyl iodide were mixtures of dimethyldiphenylphosphonium iodide and methyldiphenylphosphonium iodide. The dimethyldiphenylphosphonium iodide in each case probably arose from diphenylphosphine, although under ordinary conditions this with methyl iodide gives only methyldiphenylphosphonium iodide.

EXPERIMENTAL

Experiments involving phosphines were carried out under oxygen-free nitrogen. Unless otherwise stated, light petroleum refers to that fraction having b. p. 60—80°.

Methoxymethyldiphenylphosphine.—A suspension of methoxymethyltriphenylphosphonium chloride (50 g.) in N-sodium hydroxide (500 ml.) was refluxed for 0·5 hr., cooled, and extracted twice with benzene. The extract was dried and evaporated, and the residue crystallised from benzene–light petroleum to give *methoxymethyldiphenylphosphine oxide* (31 g.), m. p. 116—117° (Found: C, 68·2; H, 6·1. $C_{14}H_{15}O_2P$ requires C, 68·2; H, 6·1%).

The above phosphine oxide (24 g.) was added slowly to a stirred suspension of lithium aluminium hydride (8 g.) in di-n-butyl ether (200 ml.) on a boiling-water bath, the suspension was heated for 18 hr., then cooled in ice, and methanol (40 ml.) was added. Solvent was removed under reduced pressure and the residue distilled to give *methoxymethyldiphenylphosphine* (12 g.), b. p. 138—139°/0·1 mm. The *methiodide* had m. p. (from chloroform–ethyl acetate) 144—146° (Found: C, 48·45; H, 4·8. $C_{15}H_{18}IOP$ requires C, 48·4; H, 4·9%); the *benzylphosphonium bromide* had m. p. (from chloroform–ethyl acetate) 173—175° (Found: C, 63·1; H, 5·6. $C_{21}H_{22}BrOP$ requires C, 62·85; H, 5·5%).

Action of Hydrogen Bromide in Acetic Acid on Methoxymethyldiphenylphosphine.—A slow stream of oxygen-free hydrogen bromide was passed for 8 hr. through a refluxing solution of methoxymethyldiphenylphosphine (11 g.) in acetic acid (100 ml.). Solvent was then removed under reduced pressure, the residue taken up in benzene (100 ml.), methyl iodide (10 ml.) added, and the solution set aside at room temperature for 18 hr. Filtration gave dimethyldiphenylphosphonium iodide (3·2 g.), m. p. (from water) 250—251° (decomp.) (Found: C, 49·25; H, 4·8. Calc. for $C_{14}H_{16}IP$: C, 49·1; H, 4·7%). The mother-liquors, on evaporation and crystallisation of the residue from light petroleum (b. p. 80—100°), gave methyldiphenylphosphine oxide (7 g.), m. p. and mixed m. p. 112·5—113°.

Hydroxymethyldiphenylphosphine.—Diphenylphosphine (8 g.), 40% aqueous formaldehyde (15 ml.), concentrated hydrochloric acid (12 ml.), and water (40 ml.) were heated on a steam-bath for 1 hr., the clear solution cooled, and sodium iodide (15 g.) in water (10 ml.) added. The resulting syrup crystallised when rubbed with saturated aqueous sodium iodide and was filtered off and dried (13·5 g.).

The phosphonium iodide (10 g.) was dissolved in water (50 ml.), 2N-sodium hydroxide (20 ml.)

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[2] Hellman and Schumacher, *Angew. Chem.*, 1960, **72**, 211.

added, and the suspension extracted with chloroform (100 ml.). The extract was dried and evaporated to give hydroxymethyldiphenylphosphine (5·2 g.) [characterised as the *phosphine oxide*, m. p. (from benzene–light petroleum) 138—140°, $\lambda_{max.}$ 3·1, 8·65 μ (Found: C, 67·35; H, 5·75. $C_{13}H_{13}O_2P$ requires C, 67·2; H, 5·6%) and the *benzylphosphonium bromide*, m.p. (from chloroform–ethyl acetate) 220—222° (decomp.) (Found: C, 61·85; H, 5·2. $C_{20}H_{20}BrOP$ requries C, 62·0; H, 5·2%].

*Action of Toluene-*p*-sulphonic Acid in Acetic Acid on Hydroxymethyldiphenylphosphine.*—A solution of hydroxymethylphosphine (5·8 g.) and toluene-*p*-sulphonic acid (0·25 g.) in acetic acid (50 ml.) was refluxed for 6 hr., then evaporated under reduced pressure, and the residue in benzene (40 ml.) was treated with methyl iodide (5 ml.) for 3 hr. Filtration gave *acetoxymethyldiphenylphosphonium iodide* (4·25 g.), m. p. (from chloroform–ethyl acetate) 175—178°, $\lambda_{max.}$ 5·66 μ (Found: C, 47·9; H, 4·45. $C_{16}H_{18}IO_2P$ requires C, 48·0; H, 4·5%). The mother-liquors were evaporated and the residue, in chloroform, washed with sodium hydrogen carbonate solution and with water. The solution was dried and evaporated, and the residue crystallised from light petroleum (b. p. 80—100°) to give methyldiphenylphosphine oxide (2·8 g.), m. p. 111—112°.

*Action of Toluene-*p*-sulphonic Acid in Toluene on Hydroxymethyldiphenylphosphine.*—A solution of hydroxymethyldiphenylphosphine (13·5 g.) and toluene-*p*-sulphonic acid (0·25 g.) in toluene (100 ml.) was refluxed for 5·5 hr., and then distilled to give diphenylphosphine (9 g.), b. p. 150—152°/15 mm.

1-*Hydroxypropyldiphenylphosphine.*—Dry hydrogen chloride was passed through a solution of diphenylphosphine (5 g.) and propionaldehyde (5 ml.) in ether (75 ml.) at 0° until the first signs of stickiness in the resulting precipitate. Filtration then gave *di-*(1-*hydroxypropyl*)-*diphenylphosphonium chloride* (6 g.), m. p. (from ethyl acetate) 140° (decomp.) (Found: C, 64·0; H, 7·4. $C_{18}H_{24}ClO_2P$ requires C, 63·8; H, 7·1%).

The above phosphonium chloride (1·9 g.) in ethanol (20 ml.) was titrated with 2N-sodium hydroxide to pH 9, and the solution was diluted with water and extracted with chloroform. The extract was dried and evaporated. The infrared spectrum of the residue indicated that it was largely diphenylphosphine. It was taken up in acetic acid (15 ml.), toluene-*p*-sulphonic acid (0·25 g.) added, and the solution refluxed for 16 hr. Solvent was then removed under reduced pressure and the residue, in benzene (30 ml.), treated with methyl iodide (5 ml.) for 36 hr. The crude phosphonium iodide, m. p. 154—158°, was then filtered off and the filtrate washed with aqueous sodium carbonate and with water, dried, and evaporated. Crystallisation of the residue from ethyl acetate–light petroleum gave *diphenylpropylphosphine oxide* (0·45 g.), m. p. and mixed m. p. 100—101°. An authentic sample, m. p. 100—101° (Found: C, 73·6; H, 7·0. $C_{15}H_{17}OP$ requires C, 73·7; H, 7·0%), was prepared by the alkaline hydrolysis of triphenylpropylphosphonium iodide.

1-*Hydroxybutyldiphenylphosphine.*—Dry hydrogen chloride was passed through a solution of diphenylphosphine (5 g.) and butyraldehyde (7 ml.) in ether (75 ml.) at 0°, and the resulting precipitate filtered off. Crystallisation from ethyl acetate gave *di-*(1-*hydroxybutyl*)*diphenylphosphonium chloride* (8·3 g.), m. p. 127° (decomp.) (Found: C, 65·3; H, 7·6. $C_{20}H_{28}ClO_2P$ requires C, 65·4; H, 7·7%).

A solution of the above phosphonium chloride (8 g.) in water (100 ml.) was made alkaline to phenolphthalein with 2N-sodium hydroxide and extracted thrice with chloroform, and the combined extracts were dried and evaporated. The residue (4·8 g.), largely diphenylphosphine, was dissolved in acetic acid (50 ml.) with toluene-*p*-sulphonic acid (0·3 g.), and the solution was refluxed for 5 hr. Solvent was then removed under reduced pressure and the residue, in benzene (30 ml.), treated with methyl iodide (5 ml.) at room temperature overnight. The mixed phosphonium iodides, m. p. 154—158°, were filtered off and the filtrate washed twice with water, dried, and evaporated. After passage, in benzene, through a small column of alumina, the residue crystallised from ethyl acetate–light petroleum (b. p. 80—100°) to give *butyldiphenylphosphine oxide* (1·1 g.), m. p. 93—94°. An authentic sample, m. p. 93—94° (Found: C, 74·5; H, 7·35. $C_{16}H_{19}OP$ requires C, 74·3; H, 7·4%), was prepared by the alkaline hydrolysis of butyltriphenylphosphonium bromide.

The mixed phosphonium iodides, m. p. 154—158°, $\lambda_{max.}$ 4·1—4·2 μ, on crystallisation from chloroform–ethyl acetate and then from water, gave dimethyldiphenylphosphonium iodide, m. p. and mixed m. p. 250—251°. When dissolved in warm water, and the cooled solution extracted with ether, they gave methyldiphenylphosphine, identified as the allylphosphonium bromide, m. p. 167—169° (lit.,[3] m. p. 161°) (Found: C, 59·55; H, 5·7. Calc. for $C_{16}H_{18}IP$: C, 59·7; H, 5·4%).

Diphenylphosphine and methyl iodide in benzene at room temperature overnight gave *methyldiphenylphosphonium iodide*, m. p. 162—163° (Found: C, 47·7; H, 4·3. $C_{13}H_{14}IP$ requires C, 47·6; H, 4·3%).

α-Hydroxybenzyldiphenylphosphine.—Dry hydrogen chloride was passed into a solution of diphenylphosphine (5 g.) and benzaldehyde (5 g.) in ether (150 ml.), and the resulting precipitate was filtered off and crystallised from ethyl acetate–ether to give *di-(α-hydroxybenzyl)diphenylphosphonium chloride* (8·1 g.), m. p. 165—170° (Found: C, 72·3; H, 5·3. $C_{26}H_{24}ClO_2P$ requires C, 71·8; H, 5·5%).

A suspension of this phosphonium chloride (10 g.) in water (150 ml.) and chloroform (100 ml.) was shaken while 2N-sodium hydroxide was added slowly till the aqueous layer was alkaline to phenolphthalein. The chloroform was then dried and evaporated, and the residue taken up in benzene (40 ml.) and allowed to crystallise. Filtration gave α-hydroxybenzyldiphenylphosphine oxide, m. p. (from aqueous ethanol) 177—179° (lit.,[4] m. p. 178—179·5°) (Found: C, 74·1; H, 5·75. Calc. for $C_{19}H_{17}O_2P$: C, 74·0; H, 5·5%). The filtrate was evaporated and the residue, which showed no P–H absorption in the infrared spectrum, was taken up in acetic acid (40 ml.), toluene-*p*-sulphonic acid (0·25 g.) added, and the solution refluxed for 8 hr. Solvent was then removed under reduced pressure and the residue crystallised from benzene, to give benzyldiphenylphosphine oxide (2·6 g.), m. p. 195—196° (lit.,[5] m. p. 196°) (Found: C, 78·3; H, 5·9. Calc. for $C_{19}H_{17}OP$: C, 78·0; H, 5·8%).

Benzyldiphenylphosphonium Bromide.—A solution of diphenylphosphine (2 g.) and benzyl bromide (5 g.) in benzene (20 ml.) was set aside at room temperature for 5 days. The resulting sticky solid was rubbed with ethyl acetate and then crystallised from chloroform–ethyl acetate, to give *benzyldiphenylphosphonium bromide* (2·1 g.), m. p. 202—204° (Found: C, 64·3; H, 5·1. $C_{19}H_{18}BrP$ requires C, 63·8; H, 5·1%). The hydrobromide was warmed on a steam-bath with 2N-sodium hydroxide for a few minutes, and the resulting solid crystallised from aqueous ethanol to give *benzyldiphenylphosphine*, m. p. 74° (Found: C, 82·7; H, 6·4. $C_{19}H_{17}P$ requires C, 82·5; H, 6·2%). The *methiodide* had m. p. (from ethanol) 243—245° (Found: C, 57·3; H, 4·6. $C_{20}H_{20}IP$ requires C, 57·5; H, 4·8%).

Methylphenylphosphine from Phenylphosphine.—Phenylphosphine (15 g.), 40% aqueous formaldehyde (36 ml.), concentrated hydrochloric acid (30 ml.), and water (100 ml.) were heated on a steam-bath for 1 hr., and the resulting solution was cooled in ice, made alkaline to phenolphthalein with 10N-sodium hydroxide, and extracted thrice with chloroform. The extracts were dried and evaporated, the residue (19·5 g.) was dissolved in benzene (100 ml.) at 0°, methyl iodide (8 ml.) added, and the solution set aside at room temperature overnight. Solvent was then removed, the residue dissolved in water (200 ml.), and the solution made alkaline to phenolphthalein with 2N-sodium hydroxide and extracted with chloroform. The extracts were dried and evaporated, and the residue (11·5 g.), with toluene-*p*-sulphonic acid (0·3 g.), was refluxed in toluene (50 ml.) for 8 hr. Distillation then gave methylphenylphosphine (2·6 g.), b. p. 60—62°/13 mm., $\lambda_{max.}$ 4·3 μ(s). With benzyl bromide in benzene at room temperature for 4 days, this gave *benzylmethylphenylphosphonium bromide*, m. p. (from chloroform–ethyl acetate) 159—160°, $\lambda_{max.}$ 4·1—4·3 μ (Found: C, 56·85; H, 5·65. $C_{14}H_{16}BrP$ requires C, 56·95; H, 5·5%). The hydrobromide was shaken with 2N-sodium hydroxide and chloroform, the chloroform dried and evaporated, and the residue treated with methyl iodide in benzene to give *benzyldimethylphenylphosphonium iodide*, m. p. (from chloroform–ethyl acetate) 168—169° (Found: C, 50·3; H, 5·1. $C_{15}H_{18}IP$ requires C, 50·55; H, 5·1%).

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[3] Meisenheimer and Lichtenstadt, *Annalen*, 1926, **449**, 213.
[4] Miller, Miller, Rogers, and Hamilton, *J. Amer. Chem. Soc.*, 1957, **79**, 424.
[5] Michaelis and LaCoste, *Ber.*, 1885, **18**, 2109.