760. *The Mechanism of Methyl Group Migration from Oxygen to Phosphorus in* m-*Methoxyphenylphenylphosphine*

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o-, *m*-, and *p*-Methoxyphenylphenylphosphinic acids on reduction with lithium aluminium hydride in tetrahydrofuran give a mixture of the corresponding secondary methoxyphenylphenylphosphine and the tertiary methoxyphenylmethylphenylphosphine.

The *m*-methoxyphenylphenylphosphine, when converted into the phosphide ion in tetrahydrofuran, on boiling gives the isomeric *m*-hydroxyphenylmethylphenylphosphine, with intermediate formation of the above tertiary *m*-methoxyphosphine. The mechanism of these changes is discussed.

The reduction of *o*-, *m*-, and *p*-methoxyphenylphenylphosphinic acids (I) with lithium aluminium hydride in tetrahydrofuran gives rise to the corresponding secondary phosphines (II) and the tertiary methoxyphenylmethylphenylphosphines (III); the ethyl esters of the *o*- and *m*-acids (I) behave similarly. Moreover, both the *o*-methoxyphenylphenylphosphine oxide (IV) and the pure *o*-secondary phosphine (II) when treated with the hydride also give rise to the tertiary methylphosphine (III).[1] In contrast, the *m*- and *p*-ethoxyphenylphenylphosphinic acids when similarly reduced give solely the corresponding ethoxyphenylphenylphosphines [as (II)], and no tertiary phosphines.[1,2]

$\mathrm{MeO{\cdot}C_6H_4{\cdot}PPh(:O)OH}$	$\mathrm{MeO{\cdot}C_6H_4{\cdot}PPhH}$	$\mathrm{MeO{\cdot}C_6H_4{\cdot}PPh{\cdot}Me}$	$\mathrm{MeO{\cdot}C_6H_4{\cdot}PPh(:O)H}$
(I)	(II)	(III)	(IV)

The production of the tertiary methylphosphine (III) was attributed to the activity of the phosphide ion (V), which could demethylate part of the phosphine (II), undergoing

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[1] F. G. Mann, B. P. Tong, and V. P. Wystrach, *J.*, **1963**, 1155.

[2] R. C. Hinton, F. G. Mann, and D. Todd, *J.*, **1961**, 5454.

P-methylation itself to the tertiary phosphine (III). This demethylation mechanism is supported by the fact that a tetrahydrofuran solution of the diphenylphosphide ion,

$MeO{\cdot}C_6H_4{\cdot}PPh^-$ (V) $Ph_2P{\cdot}[CH_2]_4{\cdot}OH$ (VI) $HO{\cdot}C_6H_4{\cdot}PPh{\cdot}Me$ (VII) $MeO{\cdot}C_6H_4{\cdot}P(:O)MePh$ (IX)

Ph_2P^-, generated by the action of butyl-lithium on the phosphine Ph_2PH, when boiled with anisole for 4 hr. gives phenol and methyldiphenylphosphine in high yield, and when similarly boiled with phenetole gives very little reaction;[1,4] in the absence of reactive ethers, the phosphide ion attacks the boiling solvent with the formation of 4-hydroxybutyldiphenylphosphine (VI).[3] Further, diphenylphosphinic acid or its ethyl ester with lithium aluminium hydride in boiling tetrahydrofuran gives diphenylphosphine, but longer heating reduces the yield of this phosphine and increases that of the hydroxybutylphosphine (VI).[3,5]

The phosphide ion (V) therefore reacts rapidly with the methoxyl group but only slowly with tetrahydrofuran and even more slowly with the ethoxyl group; hence the negligible action of the ethoxyphenylphenylphosphide ion on the ethoxyl group during the reduction of the *m*- and *p*-ethoxy-acids [as (I)].

Since the action of lithium aluminium hydride on the methoxyphenylphenylphosphinic acids (I) involves two major processes, reduction and methyl group migration, we have investigated the mechanism of the reduction of diphenylphosphinic acid, its ethyl ester, and its aluminium salt by lithium aluminium hydride, with the intermediate formation of diphenylphosphine oxide;[5] the present Paper deals with the mechanism of the methyl group migration.

We find that the crude reduction product from *m*-methoxyphenylphenylphosphinic acid (I), obtained using lithium aluminium hydride in tetrahydrofuran, on thorough distillation gives the usual mixture of the secondary phosphine (II) and the tertiary phosphine (III), and also the higher-boiling secondary phosphine oxide (IV). The corresponding phosphine oxides have now been obtained as intermediates in the reduction of the *m*-acid (I), the diphenylphosphinic acid,[5] and the *o*-chlorophenylphenylphosphinic acid.[6]

Pure *m*-methoxyphenylphenylphosphine (II) in tetrahydrofuran was converted into the phosphide ion (V) by the addition of butyl-lithium (one equiv.) in petroleum and the solution boiled for 4 hr. Working up yielded the *m*-methoxyphenylmethylphenylphosphine (III) and the *m*-hydroxyphenylmethylphenylphosphine (VII), identified by analysis, and infrared and nuclear magnetic resonance spectra, and by conversion into the methiodide and methopicrate. The production of the tertiary phosphine (III) from the secondary phosphine (II) is therefore not peculiar to the *ortho*-series. The use of lithium aluminium hydride in place of butyl-lithium to generate the phosphide ion (V) gave the same two products with a small proportion of unchanged secondary phosphine, but the overall reaction was slower and the working up of the reaction mixture more difficult.

It is improbable that the conversion of the secondary *m*-methoxyphosphine (II) into the isomeric tertiary *m*-hydroxymethylphosphine (VII) occurs by an intramolecular reaction. There are two possible mechanisms for an intermolecular reaction. (A) Two ions (V) undergo a complete double bimolecular reaction, giving directly two molecules of the hydroxymethylphosphine (VII); this mechanism is highly improbable. (B) The two ions could interact stepwise to give the methoxymethylphosphine (III) and the doubly charged oxide-phosphide ion (VIII); the more powerful phosphide ion portion of compound (VIII) would then attack the more vulnerable methyl group of the *o*-methoxyl

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[3] K. B. Mallion and F. G. Mann, *Chem. and Ind.*, 1963, 654, 1558.

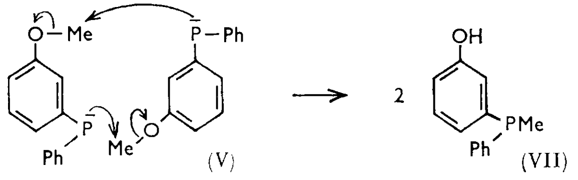
[4] F. G. Mann and M. J. Pragnell, *Chem. and Ind.*, 1964, 1386. cf. See also following Paper, No. 761.

[5] K. B. Mallion and F. G. Mann, *J.*, 1964, 6121.

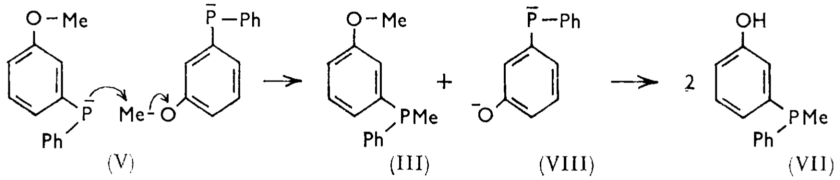
[6] M. J. Gallagher, E. C. Kirby, and F. G. Mann, *J.*, 1963, 4846.

function of compound (III), with the same final result as that in (A). This mechanism might involve some competing reactions; for example, the ion (V) might also react with the freshly formed phosphine (III), which would thus be converted into the ion corresponding to compound (VII), the ion (V) being itself converted into the phosphine (III). These are, however, alternative and possibly minor routes leading again to the final production solely of the phosphine (VII) with intermediate formation of the tertiary phosphine (III).

(A)



(B)



The significant difference in the mechanisms (A) and (B) is that the phosphine (III) is an intermediate only in mechanism (B), and could be isolated therefore if the reaction were stopped before completion. This mechanism is thus in full accord with our experimental results.

The wider application of the secondary phosphine ion as a dealkylating agent has been briefly recorded.[4]

EXPERIMENTAL

m-*Methoxyphenylphenylphosphinic Acid* (I).—This was prepared by the Doak–Freedman diazofluoroborate method, using the precautions previously recorded.[2,1]

Reduction.—The acid (I) (100 g.) in tetrahydrofuran (400 ml.) was reduced by lithium aluminium hydride (18·4 g., 1·2 mol.) under nitrogen, the product being hydrolysed and extracted with ether as before.[2,1] The dried ether extracts from two such reductions, when combined and evaporated, left a crude oil (54·2 g.), the i.r. spectrum of which showed the >P–H and >P–Me bands and a weak O–H band.

The united aqueous layers on oxidation with hydrogen peroxide and acidification gave the acid (I) (62·8 g.), m. p. 145—146·5° (from ethanol).

The crude oil, slowly distilled, gave the fractions: (i) b. p. 113—123°/0·2 mm., 22·8 g.; (ii) b. p. 123—130°/0·5 mm. (13·5 g.); (iii) b. p. 143—170°/0·4 mm., 8·0 g.; undistilled residue, 4·3 g. Fractions (i) and (ii), clear mobile oils having identical i.r. spectra, were the familiar mixture of the phosphines (II) and (III), and each with boiling methyl iodide gave *m*-methoxyphenyldimethylphenylphosphonium iodide, m. p. and mixed m. p. 129—132° (lit.,[1] 129·5—132°), i.r. spectrum identical with that of authentic iodide.

The early portion of fraction (iii) came over as a clear oil, the remainder as a cloudy viscous oil, b. p. 160—170°. On refractionation at 0·25 mm. it gave a major fraction, b. p. 152—178° (4·6 g.), of the phosphine oxide (IV). This did not give a methiodide, but a portion when suspended in aqueous sodium carbonate, treated with hydrogen peroxide, and warmed, effervesced and gave a clear solution which, when cooled and acidified, deposited the acid (I), m. p. and mixed m. p. 144·5—147°, in almost 100% yield. The residue (4·3 g.) contained *ca.* 50% of undistilled phosphine oxide (IV). [Earlier reductions [1,2] were carried out to obtain the phosphines (II) and (III), and the distillation of the crude oil was not continued beyond that of these two phosphines.]

4-Hydroxybutyl-*m*-methoxyphenylphenylphosphine [as (VI)] was not detected.

Fractions (i) and (ii), and the forerun from the refractionation of fraction (iii), united and refractionated, gave solely the mixed phosphines (II) and (III). This mixture was shaken with 5N-hydrochloric acid, and then with benzene to extract the phosphine (II); the aqueous layer was basified and shaken with benzene to extract the phosphine (III).[1] The pure phosphine (II), b. p. 130°/0·4 mm., n_D^{22} 1·6228, was used in the following experiments.

Reaction of the m-*Phosphide Ion* (V) *in Tetrahydrofuran.*—A solution of the phosphine (II) (8·2 g.) in tetrahydrofuran (80 ml.) under nitrogen was stirred while butyl-lithium (1·05 mol., 24·1 ml. of a 1·66-molar solution in petroleum) was added dropwise. The mixture became orange and almost boiled. It was then boiled under reflux for 4 hr., the colour fading considerably. Solvent (55 ml.) was removed by distillation, and the residue was cooled and treated in turn with ether (70 ml.) and water (50 ml.). The alkaline aqueous layer was extracted with ether (3 × 30 ml.), treated with 5N-hydrochloric acid to liberate tertiary phenolic phosphine, and extracted with benzene (3 × 50 ml.). The united ether layer and extracts, when washed, dried, and evaporated, gave a cloudy viscous oil (3·8 g.); the benzene layer, similarly treated, gave a clear mobile oil (3·0 g.).

A sample of the mobile oil readily gave a methiodide, m. p. 172·5—174·5° (from ethanol); the remainder on distillation gave the m-*hydroxyphenylmethylphenylphosphine* (VII) (2·5 g.), b. p. 135—142°/0·3 mm., n_D 1·6446 (Found: C, 72·05; H, 6·4; P, 13·8. $C_{13}H_{13}OP$ requires C, 72·2; H, 6·1; P, 14·3%), with negligible residue. The n.m.r. spectrum in deuterochloroform showed the P–Me doublet, complete absence of the OMe group, with aromatic peaks obscuring the phenolic OH group. The i.r. spectrum showed an OH band and a >PMe band [7] at 3400 and 880 cm.$^{-1}$, respectively.

The phosphine (VII) gave a *methiodide*, m. p. 173·5—175° (from ethanol–ether) (Found: C, 46·6; H, 4·6. $C_{14}H_{16}IOP$ requires C, 46·8; H, 4·5%), and a *methopicrate*, m. p. 180—181·5° (from ethanol) (Found: C, 52·3; H, 4·15; N, 9·0. $C_{20}H_{18}N_3O_8P$ requires C, 52·25; H, 3·9; N, 9·1%).

The presence of *m*-hydroxyphenylphenylphosphine, HO·C_6H_4·PPhH, possibly arising from the ion (VIII), could not be detected in the benzene extract; it is noteworthy that a similar examination of the aqueous layer arising from the reduction of the *o*-phosphinic acid (I) gave the corresponding crude secondary phosphine or its oxide, since on oxidation it gave pure *o*-hydroxyphenylphenylphosphinic acid.[1]

The viscous oil (3·8 g.) from the ether extract contained a mixture of the expected tertiary methoxyphosphine (III) and the hydroxyphosphine (VII), the original aqueous layer having been insufficiently alkaline to retain completely this phenolic phosphine. These two components co-distilled at 0·3 mm., and arbitrary fractions were taken: (i) b. p. 120—140° (0·9 g.), n_D^{27} 1·6280; (ii) b. p. 140—146° (1·3 g.), n_D (as before) 1·6332; (iii) b. p. 146—150° (1·1 g.), n_D 1·6362. The i.r. spectra of these fractions were virtually identical, the MeO peak at 1040 cm.$^{-1}$ however decreasing in intensity with increasing b. p. The united fractions (2·2 g.) were therefore shaken with aqueous 4N-sodium hydroxide, and the mixture again extracted with benzene. This extract on evaporation gave the phosphine (III) (0·6 g.), having an i.r. spectrum identical with that of the authentic phosphine.[1]

For complete confirmation, this phosphine in acetone was oxidised with hydrogen peroxide (100 vol.). After the vigorous reaction, the acetone was boiled off, and the cold aqueous residue (containing a heavy oil) was extracted with chloroform. This extract was shaken with 15% aqueous sodium hydroxide, washed with water, dried, and evaporated. The residue rapidly solidified and, after crystallisation from ethyl acetate–light petroleum, furnished m-*methoxyphenylmethylphenylphosphine oxide* (IX), m. p. 95—96° (Found: C, 68·3; H, 6·6. $C_{14}H_{15}O_2P$ requires C, 68·3; H, 6·2%). A sample of the oxide (IX), similarly prepared from the authentic pure phosphine (III), had m. p. and mixed m. p. 95—96°; the two samples had identical i.r. spectra.

The aqueous sodium hydroxide layer from the benzene extraction was acidified with hydrochloric acid and extracted with benzene. Evaporation of the benzene gave the hydroxyphosphine (VII) (0·9 g.); its i.r. spectrum was identical with that of the pure phosphine and

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[7] K. B. Mallion, F. G. Mann, B. P. Tong, and V. P. Wystrach, *J.*, 1963, 1327.

showed no indication of an MeO group. It gave the methiodide, m. p. 167—171°, after one recrystallisation, mixed m. p. 170—173° with the authentic methiodide.

Reaction of m-*Methoxyphenylphenylphosphine* (II) *with Lithium Aluminium Hydride.*—A stirred solution of the pure phosphine (II) (11·0 g.) in tetrahydrofuran (100 ml.) under nitrogen was treated portion-wise with the hydride (2·13 g., 1·1 mol.). The yellow-orange mixture was boiled under reflux for 4 hr., with only slight fading of the colour. The solvent (70 ml.) was distilled off, and the chilled residue treated in turn cautiously with ether (70 ml.), 20% aqueous potassium sodium tartrate (50 ml.), and finally with 16N-sodium hydroxide (50 ml.) to ensure retention in the aqueous layer of the weakly acidic phenolic phosphine (VII), with the neutral phosphine (III) in the ethereal layer. This addition, however, gave such a gelatinous sludge that no separation into two layers occurred; consequently concentrated hydrochloric acid (40 ml.) was added, giving an approximately 3·3N-sodium hydroxide solution. Manipulation of this mixture was still difficult, as a reasonably sharp separation of the ethereal and aqueous layers occurred slowly; moreover the more weakly alkaline solution did not give a sharp chemical separation of the component phosphines. The mixture was, however, worked up as in the previous experiment, the united ether extracts giving an oil (2·8 g.), and the benzene extract of the acidified residue also giving an oil (2·3 g.); these yields could undoubtedly be increased with further experience.

The oil (2·3 *g.*) *from the benzene extract.* The i.r. spectrum showed that this oil was mainly the phenolic phosphine (VII) with a small proportion of a secondary phosphine, either unchanged phosphine (II) or *m*-hydroxyphenylphenylphosphine, $HO{\cdot}C_6H_4{\cdot}PPhH$. The n.m.r. spectrum of the oil in deuteriochloroform showed the $>$P–Me doublet, a small OMe band, but no $>$PH band, although this band, being much smaller than the OMe band, might have escaped detection. The oil, when treated with boiling methanolic methyl iodide, gave a mixture of *m*-hydroxy- and *m*-methoxy-phenyldimethylphosphonium iodides. A suspension of the oil in aqueous sodium carbonate was treated with hydrogen peroxide (with evolution of heat), then concentrated and cooled; the insoluble oil was extracted with chloroform, and the aqueous residue then acidified, with deposition of a white gum which did not solidify. The chloroform extract on evaporation gave a viscous oil which could not be obtained crystalline; it must have been a tertiary phosphine oxide, almost certainly the oxide of the phenolic phosphine (VII), since that of the phosphine (III) crystallises very readily.

The oil (2·8 *g.*) *from the ether extract.* The i.r. spectrum showed this to be mainly the phosphine (III) with some unchanged phosphine (II) and possibly a trace of the phosphine (VII); the n.m.r. spectrum in deuterochloroform showed the $>$P–Me doublet, the OMe band, and one $>$P–H doublet. A portion of the oil was oxidised with hydrogen peroxide as above; the oil in the cold residue was extracted with ether, and the aqueous layer on acidification gave the phosphinic acid (I), identified by m. p. and mixed m. p. and by its i.r. spectrum, thus confirming the presence of the phosphine (II). The ether extract, when shaken with aqueous sodium hydroxide, washed, dried, and evaporated, gave the phosphine oxide (IX), similarly identified by mixed m. p. and by its i.r. spectrum, confirming the presence of the phosphine (III).

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