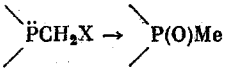
12. M. Hidai, T. Kashiwagi, T. Ikeuchi, and Y. Uchida, J. Organomet. Chem., 30, 279 (1971).

# PSEUDOALLYLIC REARRANGEMENT OF ACETOXYMETHYLPHOSPHINES

E. N. Tsvetkov, T. E. Kron,
Z. N. Mironova,* and M. I. Kabachnik

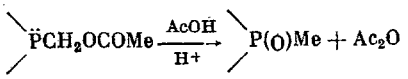
UDC 542.952.1:547.1'118

The oxidation–reduction conversion of α-substituted phosphines into the corresponding methylphosphine oxides [1], which we called a pseudoallylic rearrangement, is of interest as a method for the synthesis of substituted oxides in which the degree of functionality is a unit lower than in the initial phosphines:



This reaction is of special significance for the production of bifunctional phosphine oxides and, in particular, phosphorus-containing glycols and primarily their simplest representative, i.e., methyldi(hydroxymethyl)phosphine oxide. A series of examples of the rearrangement of hydroxyalkylphosphines have been described [2-10], but the difficulties involved in the purification of the starting materials and the final products restrict the wide use of this direct method for the production of hydroxyalkylphosphine oxides.

In the present work we studied the pseudoallylic rearrangement of acetoxymethylphosphines [11], which in contrast to hydroxymethylphosphines are easily purified by vacuum distillation. It was shown that this reaction can be used successfully for the production of acetoxymethyl and the corresponding hydroxymethylphosphine oxides:



Tri(acetoxymethyl)phosphine [11] is converted with a high yield into methyldi(acetoxymethyl)phosphine oxide (I) (Table 1) when heated with glacial acetic acid at 180-190°C for 8 h in the presence of acidic catalysts [14] [ a 6% solution of dry hydrogen chloride in glacial acetic acid; p-toluenesulfonic acid (monohydrate); and 90% phosphoric acid]. Increase in the content of hydrogen chloride leads to contamination of the oxide (I) with the products from substitution of the acetoxy groups by chlorine atoms. The most suitable of the given catalysts is p-toluenesulfonic acid. In the absence of the catalyst the rearrangement is not observed under the above-mentioned conditions, but it takes place under more drastic conditions (250°C, 20 h). However, the process is accompanied by such strong resinification that the product, which according to PMR data contains 95-100% of the oxide (I), can only be isolated with a yield of 40%. The reaction is accelerated by potassium acetate to a smaller degree than by acidic catalysts: according to PMR data only 30% of the tri(acetoxymethyl)phosphine rearranges after 8 h at 180-190°C.

The oxides (II-VI) (Table 1) were obtained similarly by rearrangement of the corresponding alkyldi(acetoxymethyl)- and dialkylacetoxymethylphosphines, which occurs under rather milder conditions. The synthesis of the initial compounds was described earlier [11] except for methyl- and methoxymethyldi(acetoxymethyl)phosphines (VII) and (VIII). The latter were obtained by alkylation of tri(acetoxymethyl)phosphine with dimethyl sulfate and methyl chloromethyl ether respectively followed by alkaline decomposition of the phosphonium salts which form. The synthesis of the phosphine (VII) was realized also by reduction of methyldi(acetoxymethyl)phosphine oxide by trichlorosilane. The hydroxymethyl derivatives

*Deceased.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Institute of Inorganic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1859-1862, August, 1979. Original article submitted April 24, 1978.

 0568-5230/79/2808-1722$07.50 

TABLE 1. The Yields, Constants, and Analytical Data of the Obtained Compounds

| Compound | Formula | Yield, % | bp, °C (p, mm Hg) | $n_D^{20}$ | $d_4^{20}$ | MR found | MR calc. | Found, % C | Found, % H | Found, % P | Molecular formula | Calculated, % C | Calculated, % H | Calculated, % P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (I) | $MeP(O)(CH_2OCOMe)_2$ [12] | 84 (A) | 150–151 (2) | 1,4696 | 1,2310 | 47,14 | 46,54 | | | | | | | |
| | | 90 (B) | 153–154 (2) | 1,4698 | 1,2306 | 47,15 | 46,54 | | | | | | | |
| | | 83 (C) | 149–150 (2) | 1,4705 | 1,2310 | 47,22 | 46,54 | | | | | | | |
| (II) | $Me_2P(O)CH_2OCOMe$ | 86 | 118–119 (3) | mp 77–78° (AcOEt – hexane) | | | | 40,1 | 7,5 | 20,5 | $C_5H_{11}PO_3$ | 40,0 | 7,4 | 20,6 |
| (III) | $Me(MeOCH_2)P(O)CH_2OCOMe$ | 60 | 119–122 (1) | 1,4627 | 1,1734 | 42,27 | 41,92 | 40,2 | 7,3 | 17,2 | $C_6H_{13}PO_4$ | 40,0 | 7,3 | 17,2 |
| (IV) | $Me(Bu)P(O)CH_2OCOMe$ | 91 | 144–145 (3) | 1,4614 | 1,0598 | 49,80 | 49,61 | 50,2 | 8,8 | 16,2 | $C_8H_{17}PO_3$ | 50,0 | 8,9 | 16,1 |
| (V) | $Me(Am)P(O)CH_2OCOMe$ | 87 | 130–132 (1) | 1,4620 | 1,0414 | 54,43 | 54,23 | 52,3 | 9,3 | 14,8 | $C_9H_{19}PO_3$ | 52,4 | 9,3 | 15,0 |
| (VI) | $Me(Am)_2P(O)$ | 89 | 116–117 (1) | mp 43–45° * | | | | 64,6 | 12,3 | 15,3 | $C_{11}H_{25}PO$ | 64,7 | 12,3 | 15,2 |
| (VII) | $MeP(CH_2OCOMe)_2$ | 75 (A) | 77–78 (1) | 1,4676 | 1,1164 | 47,83 | 48,07 | | | | | | | |
| | | 71 (B) | 83–83,5 (3) | 1,4734 | 1,1154 | 48,39 | 48,07 | 43,8 | 6,8 | 16,0 | $C_7H_{13}PO_4$ | 43,8 | 6,8 | 16,1 |
| (VIII) | $MeOCH_2P(CH_2OCOMe)_2$ | 69 | 95–96 (1) | 1,4719 | 1,1443 | 54,39 | 54,34 | 43,2 | 7,0 | 14,0 | $C_8H_{15}PO_5$ | 43,2 | 6,8 | 13,9 |
| (IX) | $MeP(O)(CH_2OH)_2$ | 90 | | (CH$_3$CN–MeOH) mp 77,5–79° † | | | | | | | | | | |
| (X) | $Me_2P(O)CH_2OH$ | 75 | 149–151 (1) | mp 81,5–82,5° ‡ (AcOEt) | | | | | | | | | | |

*Thermometer in the mass.

†Published data [6]: mp 60°; [8]: 68-69°.

‡Published data [7]: mp 75-78°; [8]: bp 138-140° (0.2 mm Hg), mp 74-77°; [13]: mp 75-77°.

(IX) and (X) were obtained by hydrolysis of methyldi(acetoxymethyl)- and dimethylacetoxymethylphosphine oxides (I) and (II). Their melting points were somewhat higher than those described in the literature, and this indicates higher purity. The yields, constants, and analytical data of the synthesized compounds are given in Table 1.

It should be noted that the rearrangement of acetoxymethylphosphines is the reverse of the well-known Pummerer reaction in the sulfoxide series [15]:

$$RS(O)Me \xrightarrow{Ac_2O} RSCH_2OCOMe + AcOH$$

## EXPERIMENTAL

All the operations with the trivalent phosphorus compounds were carried out in an atmosphere of argon. The PMR spectra were recorded on a Perkin–Elmer R-32 instrument (90 MHz) with HMDS as standard.* The $^{31}P-\{H\}$ NMR spectra were recorded on a Bruker HX-90 spectrometer at 36.43 MHz by a pulsed technique with 85% phosphoric acid as standard. The melting points were measured by shortened Anschutz thermometers. Corrections were not made for the protruding mercury column in the determination of the boiling points.

Methyldi(acetoxymethyl)phosphine Oxide (I). Method A. A mixture of 5.0 g of tri(acetoxymethyl)phosphine and 6 ml of glacial acetic acid, containing 6% of dry hydrogen chloride, was heated in a sealed tube in an autoclave at 200°C (bath temperature) for 5 h. The readily boiling products were removed under vacuum, and the residue was distilled. The yield of (I) was 3.5 g. PMR spectrum (δ, ppm): 1.5 d (Me–P, $J_{HP}$ = 13 Hz), 2.1 s (MeCO), 4.4 d ($CH_2$, $J_{HP}$ = 5 Hz). $^{31}P$ NMR spectrum (δ, ppm): –36.1.

Method B. A mixture of 51.5 g of tri(acetoxymethyl)phosphine, 3.9 g of p-toluenesulfonic acid (monohydrate), and 18 ml of glacial acetic acid was boiled at 180–190°C (bath temperature) for 8 h. The readily boiling products were removed under vacuum, and the residue was distilled. The yield of (I) was 38.4 g.

Method C. The oxide (I) was obtained by method B from 20.0 g of tri(acetoxymethyl)-phosphine and 6 ml of glacial acetic acid (7 h, 180–190°C) but in the presence of 1.1 g of 90% phosphoric acid. The yield of (I) was 13.8 g.

Dimethylacetoxymethylphosphine Oxide (II). The oxide (II) was obtained similarly to (I) (method B) from methyldi(acetoxymethyl)phosphine (VII) (6 h, 140–150°C). The compound was hygroscopic. PMR spectrum (δ, ppm, in chloroform): 1.6 d (Me–P, $J_{HP}$ = 13 Hz), 2.2 s (MeCO), 4.4 d ($CH_2$, $J_{HP}$ = 6 Hz). $^{31}P$ NMR spectra (δ, ppm, in chloroform): –38.9.

Methylmethoxymethylacetoxymethylphosphine Oxide (III). The oxide (III) was obtained similarly to (I) (method B) from methoxymethyldi(acetoxymethyl)phosphine (VIII) (6 h, 185–190°C, bath temperature). PMR spectrum (δ, ppm): 1.5 d (Me–P, $J_{HP}$ = 13 Hz), 2.1 s (MeCO), 3.4 s (MeO), 3.8 d ($CH_2O$–CO, $J_{HP}$ = 5.6 Hz), 4.4 d ($CH_2O$, $J_{HP}$ = 5.1 Hz). $^{31}P$ NMR spectrum (δ, ppm): –35.9.

Methylbutylacetoxymethylphosphine Oxide (IV). A mixture of 9.5 g of butyldi(acetoxymethyl)phosphine and 20 ml of glacial acetic acid, containing 6% of hydrogen chloride, was boiled for 9 h. The readily boiling products were removed under vacuum, and the residue was distilled. The yield of (IV) was 7.1 g.

Methylamylacetoxymethylphosphine Oxide (V). The oxide (V) was obtained similarly to (IV) from amyldi(acetoxymethyl)phosphine.

Methyldiamylphosphine Oxide (VI). The oxide (VI) was obtained similarly to (I) (method A) from diamylacetoxymethylphosphine (5 h, 150°C). The compound was hygroscopic.

Methyldi(acetoxymethyl)phosphine (VII). Method A. To 57.8 g of tri(acetoxymethyl)phosphine we added dropwise with stirring 32.1 g of dimethyl sulfate at 50°C. The mixture was kept at 50°C for 1 h. To the obtained salt we added 25 ml of water and 100 ml of benzene. We then added dropwise with stirring a 40% solution of sodium hydroxide to an alkaline reaction (with phenolphthalein, 10–15°C). The organic layer was removed, and the aqueous

*In cases where the solvent is not indicated the spectra are given for the individual substances.

layer was extracted with benzene. The combined extract was dried with sodium sulfate and evaporated under vacuum. The residue was distilled. The yield of (VII) was 32.4 g. PMR spectrum (δ, ppm): 1.1 d (Me—P, $J_{HP}$ = 10 Hz), 2.1 s (MeCO), 4.5 d ($CH_2$, $J_{HP}$ = 6 Hz). $^{31}P$ NMR spectrum (δ, ppm): 42.2.

Method B. To a solution of 74.0 g of methyldi(acetoxymethyl)phosphine oxide in 200 ml of absolute benzene we added dropwise 108 ml of trichlorosilane. The mixture was boiled for 3 h, the solvent was distilled, and the residue was decanted with the precipitate, dissolved in benzene, and added dropwise to a saturated solution of sodium bicarbonate. The organic layer was removed, and the aqueous layer was extracted with benzene. The combined extract was evaporated under vacuum, and the residue was distilled. The yield of (VII) was 47.9 g.

Methoxymethyldi(acetoxymethyl)phosphine (VIII). The phosphine (VIII) was obtained similarly to (VII) (method A) from tri(acetoxymethyl)phosphine and methyl chloromethyl ether (30 min at 60°C). PMR spectrum (δ, ppm): 2.0 s (MeCO), 3.3 s (MeO), 3.8 d ($CH_2$—P, $J_{HP}$ = 6 Hz), 4.5 d ($CH_2OCO$, $J_{HP}$ = 4 Hz). $^{31}P$ NMR spectrum (δ, ppm): 34.0.

Methyldi(hydroxymethyl)phosphine Oxide (IX). A mixture of 6.9 g of methyldi(acetoxymethyl)phosphine oxide and 20 ml of a 12% solution of dry hydrogen chloride in methanol was boiled for 5 h and evaporated under vacuum. The residue was dissolved in alcohol and neutralized with sodium bicarbonate. The precipitate was filtered off, and the solvent was removed under vacuum. The product was kept at 30°C over phosphorus pentoxide in a vacuum of 1-2 mm Hg for 3 h and crystallized by cooling to −70°C and gradually raising the temperature to 20°C. The yield of (IX) was 3.7 g. The compound was hygroscopic. PMR spectrum (δ, ppm, in $D_2O$): 1.8 d (Me—P, $J_{HP}$ = 13 Hz), 4.3 d ($CH_2$—P, $J_{HP}$ = 3 Hz), 4.9 s (OH). $^{31}P$ NMR spectrum (δ, ppm, in DMSO): −43.3.

Dimethylhydroxymethylphosphine Oxide (X). A 4.0-g sample of potassium hydroxide and then 8.9 g of dimethylacetoxymethylphosphine oxide were dissolved in 40 ml of absolute methanol. After 1 h at 25°C the solvent was distilled. The residue was dissolved in acetone and neutralized with concentrated hydrochloric acid. The precipitate was filtered off, the solvent was removed under vacuum, and the residue was distilled. The yield of (X) was 5.0 g. The compound was hygroscopic. PMR spectrum (δ, ppm, in chloroform): 1.5 d (Me—P, $J_{HP}$ = 16 Hz), 3.8 t ($CH_2$—P, $J_{HP}$ = 4 Hz), 6.1 q (OH, J = 4 Hz). $^{31}P$ NMR spectrum (δ, ppm, in chloroform): −45.6.

The authors express their gratitude to P. V. Petrovskii and A. I. Lutsenko for recording the NMR spectra.

## CONCLUSIONS

When heated with glacial acetic acid in the presence of acidic catalysts, acetoxymethylphosphines $\rangle PCH_2OCOMe$ rearrange to the corresponding methylphosphine oxides $\rangle P(O)Me$.

## LITERATURE CITED

1. M. I. Kabachnik and E. N. Tsvetkov, Dokl. Akad. Nauk SSSR, 143, 592 (1962).
2. S. A. Buckler and M. Epstein, J. Am. Chem. Soc., 82, 2076 (1960).
3. S. A. Buckler and M. Epstein, Tetrahedron, 18, 1211, 1221 (1962).
4. M. Epstein and S. A. Buckler, Tetrahedron, 18, 1231 (1962).
5. H. Hellman, J. Bader, H. Birkner, and O. Schumacher, Liebigs. Ann. Chem., 659, 49 (1962).
6. M. Reuter and C. Beerman, German Patent Nos. 2313307, 2319043; Ref. Zh. Khim., 14N117P, 118P (1975).
7. M. Reuter and W. Rupp, German Patent Nos. 2357276, 2357279; Ref. Zh. Khim., 2N102P, 103P (1976).
8. B. Lippsmeier, K. Hestermann, and J. Heymer, German Patent No. 2407460; Ref. Zh. Khim., 13N134P (1976).
9. A. N. Pudovik, G. V. Romanov, and V. M. Pozhidaev, Zh. Obshch. Khim., 47, 719 (1977).
10. E. Evangelidon-Tsolig and F. Ramirez, Phosphorus, 4, 121 (1974).
11. Z. N. Mironova, E. N. Tsvetkov, A. V. Nikolaev, and M. I. Kabachnik, Zh. Obshch. Khim., 37, 2747 (1967).
12. E. N. Tsvetkov, G. Borisov, Kh. Sivriev, R. A. Malevannaya, and M. I. Kabachnik, Zh. Obshch. Khim., 40, 285 (1970).

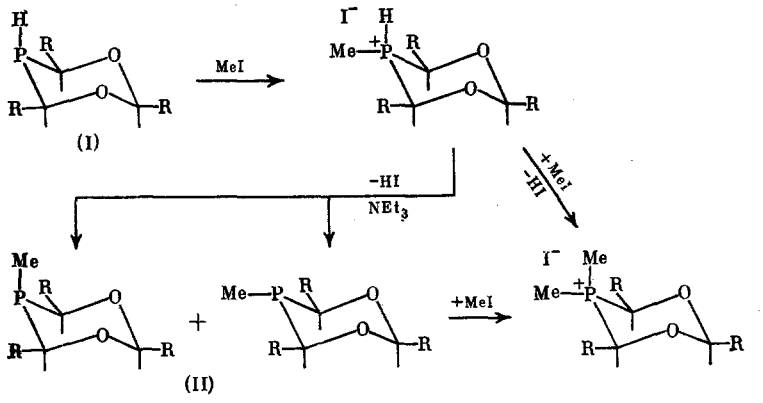
13. A. B. Bruker, E. I. Grinshtein, Kh. R. Raver, L. D. Balashova, and L. Z. Soborovskii, Collection: Chemistry and Application of Organophosphorus Compounds (Proceedings of Third Conference) [in Russian], Nauka (1972), p. 285.
14. E. N. Tsvetkov, T. E. Kron, and M. I. Kabachnik, Inventor's Certificate No. 578316, 1976; Byull. Izobr., No. 40 (1977).
15. S. Oae, Chemistry of Organosulfur Compounds [Russian translation], Khimiya (1975).

# REACTION OF 2,4,6-TRIISOPROPYL-1,3,5-DIOXAPHOSPHORINANE WITH METHYL IODIDE

B. A. Arbuzov, O. A. Erastov,
S. N. Ignat'eva, T. A. Zyablikova,
and R. P. Arshinova

UDC 542.91:547.1'118

Earlier we showed that 2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (I) exists as one stereoisomer having the chair conformation and equatorial (e) isopropyl groups and an axial ($a$) hydrogen atom at the phosphorus [1]. It therefore seemed of interest to consider the stereospecificity of addition of methyl iodide to (I) and the degree of alkylation. The reaction of methyl iodide with mono-n-alkylphosphines stops at the formation of dimethylalkylphosphonium iodides as a result of the small degree of dissociation of the product [2]. The addition of alkyl halides to trialkylphosphines is stereospecific [3]. In the light of these data it could be expected that methyl iodide would add stereospecifically to (I) and that alkylation would be incomplete.




R = $(CH_3)_2CH$

The reaction of (I) with methyl iodide was realized in benzene at 20°C for 20-48 h with the reagents in ratios between 1:1 and 1:6. The $^{31}P$ NMR spectra of the reaction mixture, of 5-methyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (II), and of a solution of (II) in methyl iodide [the methiodide (II)] are given in Fig. 1. From the spectra it is seen that alkylation does not stop at the first stage. In addition to the product from addition of one molecule of methyl iodide to (I), the product from displacement of HI by another molecule of methyl iodide is formed. The reaction of (I) with an excess of methyl iodide only gives the fully alkylated product, i.e., exhaustive alkylation is observed. In contrast to the hydriodides of aliphatic phosphines, the hydriodide (II) dissociates fairly readily. The elimination of HHal is an essential condition for the addition of the next molecule of the alkyl halide during the alkylation of phosphines [2]. Electrophilic attack by methyl iodide at the phosphorus atom of the phosphorinane (I) can only occur in one direction. The stereospecificity of the reaction therefore depends on the rate of exchange by the protons of the molecules of the hydriodide (II); if the rate is high, two stereoisomers will be obtained.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1863-1866, August, 1979. Original article submitted April 4, 1978.

 0568-5230/79/2808-1726$07.50 