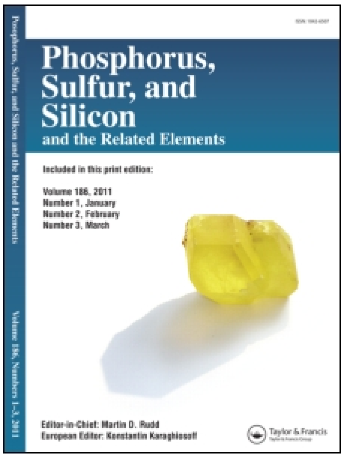

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REARRANGEMENT OF TETRAKIS(HYDROXYMETHYL)-PHOSPHONIUM CHLORIDE UPON ACID HYDROLYSIS

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Tetrakis(hydroxymethyl)phosphonium chloride (**2**) rearranges to bis(hydroxymethyl)methylphosphine oxide (**3**) upon acid hydrolysis. The extent of rearrangement increases with acid strength, but the product is apt to undergo further reaction, losing one or both of its hydroxyl functions.

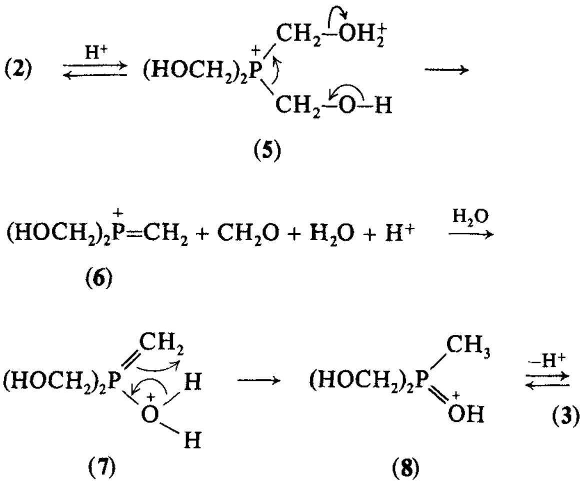
INTRODUCTION

We reported recently that the hydrolysis of tetrakis(*N*-carbomethoxylaminomethyl)phosphonium chloride (**1**) with constant-boiling hydrochloric acid gave tetrakis(hydroxymethyl)phosphonium chloride (**2**) in 68% yield, together with a small amount (7%) of bis(hydroxymethyl)methylphosphine oxide (**3**).[2] The source of the **3** is now confirmed to be **2**. Hydrolysis of **2** with constant-boiling hydrochloric acid for 20 h at 110°C gives a 6% yield of **3**, together with 82% of unreacted **2** (Eq. 1).

$$\underset{(2)}{(HOCH_2)_4PCl} \longrightarrow \underset{(3)}{(HOCH_2)_2P(O)CH_3} + CH_2O + HCl \quad (1)$$

Hydrolysis of **2** with base gives tris(hydroxymethyl)phosphine (**4**),[3,4] which is known to rearrange to **3** after prolonged heating at 120°C or above in the presence of a high-boiling solvent.[5,6] The rearrangement is catalyzed by acids.[6,7] The dissociation of **2** to **4** is, however, repressed by acids such as hydrochloric acid,[8,9] and no trace was found of either **4** or its oxidation product, tris(hydroxymethyl)phosphine oxide, in the reaction reported here.

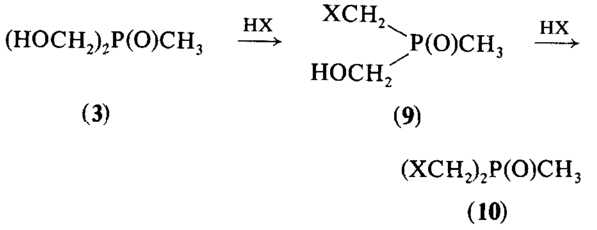
A mechanism can be written that gives **3** without recourse to **4**. Forced protonation of **2** gives the dication **5**, which dissociates to the phosphinium ion **6** with the elimination of formaldehyde. Attack of water on phosphorus gives the oxyphosphine ylene **7**, which rearranges to the phosphine oxide salt **8**. The latter yields **3** upon the loss of a proton.[10]



RESULTS AND DISCUSSION

Addition of magnesium chloride to the solution of **2** in constant-boiling hydrochloric acid raised the yield of **3** from 6% to 12%. The acidity of hydrochloric acid (pK_a −7·0)[11] is increased by salts such as magnesium chloride.[12]

Hydrolysis of **2** with constant-boiling hydrobromic acid (pK_a–9.5)[11] for 16 h at 126°C gave only 12% of unreacted **2**. The tertiary phosphine oxide fraction, neutralized with sodium bicarbonate,[13] was a mixture of 62% of **3** and 23% of (bromomethyl)-(hydroxymethyl)methylphosphine oxide (**9a**). The absence of any bis(bromomethyl)methylphosphine oxide (**10a**) was verified by extraction with methylene chloride, in which **10a** is known to be soluble.[14]



$$(HOCH_2)_2P(O)CH_3 \xrightarrow{HX} (XCH_2)(HOCH_2)P(O)CH_3 \xrightarrow{HX} (XCH_2)_2P(O)CH_3$$

(3) (9) (10)

a, X = Br
b, X = I
c, X = OAc
d, X = OC(O)NHPh

The bromine in the tertiary phosphine oxide mixture was removed by shaking with ethanolic potassium hydroxide, giving **3** in 85% yield. For confirmation of its structure, the product was converted to the bis(phenyl carbamate) **10d** by reaction with phenyl isocyanate.[5]

Hydrolysis of **2** with constant-boiling hydriodic acid (pK_a −10)[11] under the same conditions gave 23% of unreacted **2** and 37% of bis(iodomethyl)-methylphosphine oxide (**10b**), mp 176–177°C.[15]

Hydrolysis of **2** with *p*-toluenesulfonic acid in glacial acetic acid for 6 h at reflux (Trippett's reaction conditions)[16] gave 88% of unreacted acetate-free **2**.[17] The neutral fraction was a mixture of 8% of **3** and 2% of (acetoxymethyl)(hydroxymethyl)methylphosphine oxide (**9c**),[6] contaminated with the catalyst. There was no evidence of any diacetate.[18] *p*-Toluene-sulfonic acid has a pK_a of only −0.53 in water,[19] but in glacial acetic acid it is reported to be a strong acid, comparable to hydrogen chloride.[20]

In conclusion, **2** rearranges to **3** upon prolonged heating with strong acids, but the product is apt to undergo further substitution.

TABLE I
Hydrolysis of **2** with Acids

Acid	Products, % yield		
	2	**3**	Other
18% HCl	82	6	
18% HCl ($MgCl_2$)[a]	85	12	
47% HBr[b]	12	62	23 (**9a**)
51% HI[b]	23	0	37 (**10b**)
p-Toluenesulfonic Acid[c]	88	8	2 (**9c**)

[a] Hexahydrate, 2.03 g (0.01 mol).

[b] 100 ml.

[c] 0.30 g of *p*-toluenesulfonic acid in 50 ml of glacial acetic acid.

EXPERIMENTAL[21]

Melting points were corrected. IR spectra were recorded on a Perkin–Elmer 137B with NaCl optics; *s* = strong, *m* = medium. ^1H nmr spectra were recorded on a Varian A-60 using DSS as the internal reference, and ^{31}P nmr spectra on a Varian HA-60-IL at 24.3 MHz using 85% H_3PO_4 as the external reference; *s* = singlet, *d* = doublet. Chemical shifts downfield of the reference are positive, in accord with the new IUPAC sign convention.

General Procedure

Hydrochloric acid A solution of 9.53 g (0.05 mol) of **2** in 250 ml of 18% hydrochloric acid was heated to reflux under argon in an oil bath, held at 110°C for 20 h, and then stripped under vacuum. The residue (8.98 g) was taken up in 10 ml of water and transferred to a 19 × 600 mm chromatographic column containing 50 g of Bio-Rad AG50W-X4 cation exchange resin, which had been thoroughly backwashed with water and rinsed until the effluent was neutral and chloride-free. The column was eluted first with water to displace neutral compounds and HCl, and then with 18% HCl to displace the unreacted phosphonium salt. About 300 ml of each effluent was collected. The neutral fraction, stripped under vacuum, left 0.37 g (6%) of a colorless oil consisting solely of the tertiary phosphine oxide **3**: ir (neat) 1150s (P=O) and 1290m ($P-CH_3$) cm^{-1}; ^1H nmr (D_2O) δ 1.61 (d, 3H, CH_3, J = 13.0 Hz) and 4.09 (d, 4H, CH_2, J = 3.5 Hz) ppm. The phosphonium salt fraction, stripped under vacuum and rinsed with 2-propanol, yielded 7.79 g (82%) of the crystalline phosphonium salt **2**.

Hydrobromic acid The tertiary phosphine oxide fraction (7.44 g), neutralized with 1*N* sodium bicarbonate, yielded 1.32 g (26%) of sodium bromide and 6.00 g of a colorless oil which was found by ^1H nmr to be 62:23 mixture of **3** and **9a**. For **9a** (a new compound), ^1H nmr (D_2O) δ 1.72 (d, 3H, CH_3, J = 13.0 Hz), 3.68 (d, 2H, CH_2Br, J = 5.0 Hz) and 4.15 (d, 2H, CH_2O, J = 3.5 Hz) ppm. Extraction of the oil with methylene chloride failed to yield any **10a**. The oil was then shaken with a slight excess of 0.5*N* ethanolic potassium hydroxide, filtered, and stripped under vacuum, giving 5.27 g (85%) of **3**: ir, ^1H nmr as above; ^{31}P nmr (D_2O) δ 52.4 (quartet of quintets, J = 13.3 ($P-CH_3$) and 3.2 (PCH_2) Hz; lit.[6, 22] 50.4 to 50.7 ppm).

For confirmation of its structure, the product was converted to the bis(phenyl carbamate) **10d**, mp 172–173°C (lit.[5] mp 172°C) by reaction with phenyl isocyanate in acetonitrile. Acetone (15 ml/g) is a more convenient solvent for the recrystallization of **10d** than ethanol (2 ml/g)[5] or dioxane/heptane.[23]

Hydriodic acid The tertiary phosphine oxide fraction (13.50 g) neutralized with 1*N* sodium bicarbonate, yielded 4.42 g (59%) of sodium iodide and 6.39 g (37%) of **10b**, mp 176–177°C after recrystallization from ethanol (lit.[15] mp 176–177°C from aqueous DMF): ir (Nujol) 1165s (P=O) and 1290m ($P-CH_3$) cm^{-1}.

p-Toluenesulfonic acid The tertiary phosphine oxide fraction (1.38 g), analyzed by ^1H nmr, was found to be a mixture of 0.50 g (8%) of **3**, 0.18 g (2%) of **9c**, and 0.30 g of *p*-toluenesulfonic acid,[24] together with acetic acid and other impurities. For **9c**, a liquid[6], ^1H nmr (D_2O) δ 1.67 (d, 3H, PCH_3, J = 13.0 Hz), 2.18 (s, 3H, CCH_3), 4.19 (d, 4H, PCH_2, J = 3.5 Hz) and 4.60 (d, 2H, CH_2OAc, J = 5.0 Hz) ppm.

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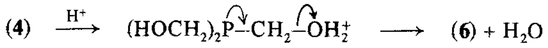
REFERENCES AND NOTES

1. One of the facilities of the Southern Region, Science and Education Administration, U.S. Department of Agriculture.
2. A. W. Frank and G. L. Drake, Jr., *J. Org. Chem.* **42**, 4040 (1977).
3. K. A. Petrov, V. A. Parshina and M. B. Luzanova, *Zh. Obshch. Khim.* **32**, 553 (1962).
4. M. Grayson, *J. Am. Chem. Soc.* **85**, 79 (1963).
5. M. Reuter and C. Beermann, *Ger. Patent* 2,313,307 to Farbwerke Hoechst A.-G. (1974); *Chem. Abstr.* **82**, 57949 (1975).
6. K. C. Lin, *U.S. Patent* 3,732,316 to Hooker Chemical Corp. (1973); *Chem. Abstr.* **79**, 67335 (1973).
7. J. H. Bright, *U.S. Patent* 4,049,719 to American Cyanamid Co. (1976); *Chem. Abstr.* **86**, 55579 (1977).
8. H. Hellmann, J. Bader, H. Birkner and O. Schumacher, *Justus Liebigs Ann. Chem.* **659**, 49 (1962).
9. (a) A. W. Frank and G. L. Drake, Jr., *Text. Res. J* **43**, 633 (1973); (b) A. W. Frank, *Text. Res. J.* **47**, 60 (1977).
10. A similar mechanism can be written for the acid-catalyzed rearrangement of **4** to **3**. Protonation of **4** gives a cation which dissociates to the phosphinium ion **6**. Attack of water on phosphorus then gives **7**, **8**, and ultimately **3**. Attack of water on carbon, reversing the dissociation, is much less favourable because of the strong tendency of phosphorus to form a resonance-stabilized P=O bond.



$$(\mathbf{4}) \xrightarrow{H^+} (HOCH_2)_2P\text{—}CH_2\text{—}OH_2^+ \longrightarrow (\mathbf{6}) + H_2O$$

11. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text* (Wiley-Interscience, New York, 1972), 3rd edn., p. 169.
12. C. H. Rochester, *Acidity Functions* (Academic Press, New York, 1970), p. 102.
13. HBr shows a greater tendency than HCl to form salts with tertiary phosphine oxides; see H. R. Hays and D. J. Peterson, *Organic Phosphorus Compounds*, G. M. Kosolapoff and L. Maier, eds. (Wiley-Interscience, New York, 1972), p. 389. Prior to neutralization, the P=O band in the IR spectrum of the mixture of **3** and **9a** was very weak, and a strong band was present at 1700 cm^{-1}, corresponding to P=OH in the tertiary phosphine oxide salt **8**.
14. O. A. Raevskii, A. N. Vereshchagin, Yu. A. Donskaya, F. G. Khalitov and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 787 (1974).
15. L. H. Chance, D. J. Daigle and G. L. Drake, Jr., *J. Chem. Eng. Data* **12**, 282 (1967).
16. S. Trippett, *J. Chem. Soc.* 2813 (1961).
17. Tetraacetate: Z. N. Mironova, E. N. Tsvetkov, A. V. Nikolaev and M. I. Kabachnik, *Zh. Obshch. Khim.* **37**, 2747 (1967).
18. Diacetate: E. N. Tsvetkov, G. Borisov, Kh. Sivriev, R. A. Malevannaya and M. I. Kabachnik, *Zh. Obshch. Khim.* **40**, 285 (1970).
19. K. Ochiai and K. Seto, *J. Nucl. Sci. Technol.* 330 (1971); *Chem. Abstr.* **75**, 87679 (1971).
20. I. M. Kolthoff and S. Brukenstein, *J. Am. Chem. Soc.* **78**, 1 (1956).
21. Naming of firms or their products in this paper does not imply their endorsement by the U.S. Department of Agriculture.
22. J. G. Colson and D. H. Marr, *Anal. Chem.* **45**, 370 (1973).
23. R. K. Valetdinov, Sh. I. Zaripov and M. Kh. Kasanov, *Zh. Obshch. Khim.* **43**, 1029 (1973).
24. *Sadtler Standard Spectra* (Sadtler Research Laboratories, Philadelphia, Pa.): ir no. 22010, nmr no. 10259.